





**H.P. CADY**

**GENERAL CHEMISTRY**

## PREFACE

This book is something of an abridgment and much of a simplification of the author's earlier book entitled "Inorganic Chemistry." It is intended for classes which have less time to devote to the subject than those for whom the former book was prepared. In it the author has preserved the general arrangement and spirit of the "Inorganic Chemistry," and has avoided a long more or less theoretical introduction, developing the subject as logically as possible from the descriptive and experimental side; each law and theory has been presented at the point which seems best fitted both to the student and to the subject.

Perhaps the most marked difference from the former book is to be found in the treatment of the atomic theory. The author feels that the recent advancements have justified a more unqualified support of this theory than was accorded it in the former work. By introducing an experimental conception of molar weights before taking up the chapter on atomic weights, the author feels that he has been able to develop the conception of atomic weights in a very simple manner from the experimental standpoint. The theory is then brought in as an explanation for the facts previously discussed.

In the preparation of the present book, the author has gladly availed himself of all the suggestions which have come to him from others who have had experience with his former book. He feels very grateful to Dr. Paul V. Faragher for advice in some difficult places, and especially so to his wife, Stella G. Cady, for loyal assistance in preparing the manuscript and reading the proof.

HAMILTON P. CADY.

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# GENERAL CHEMISTRY

## CHAPTER I

### INTRODUCTION

Chemistry is a branch of natural science and deals principally with the properties of substances, the changes which they undergo, and the natural laws which describe these changes.

It is a very difficult matter to convey thought from one person to another by means of words, and anything like accuracy can only be attained when the words have as nearly as possible the same meaning to each. For this reason it is necessary to discuss at some length the significance, in connection with chemistry, of some of the terms used in the opening statement.

**Properties of Substances.**—We are able to perceive objects around us. Each of these objects is called a body and the signs by which it makes its presence known to us are called the properties of the body. When we find ourselves surrounded by a number of different bodies we instinctively begin to arrange them into groups according to certain points of similarity in their properties. We may for example form a class of bodies called bottles and group together all objects having the general shape of bottles. When we come to examine the different members of the class, we find that they possess marked differences in properties, other than those of shape or size. Accordingly, we at once set up a number of sub-classes such as glass bottles, stoneware bottles, rubber bottles, etc., and say that these differ because they are made of different substances. Substances then, are the things of which bodies are made. As examples of substances we may give iron, salt, sugar, lead, etc.

It now remains to distinguish between the properties of bodies and those of substances. This distinction may be brought out by considering what we do in forming the sub-class glass bottles.

In grouping the glass bottles together, we pay slight attention to the properties of shape and size, but look to other characteristics which we say are the properties of the substance **glass**. Every part of a glass bottle presents the properties of the substance **glass**, and to precisely the same degree as every other part; further, if the bottle be broken into pieces, that body will cease to exist and in its place there will be a collection of bodies called pieces of glass. If we neglect shape and size, the properties of all these bodies are alike and identical with those of the **glass** bottle from which they are formed. The properties of bodies, then, aside from those of shape and size are the properties of the substance from which the bodies are made. The properties of the body, as such, are those of shape and size. A given body cannot be a barrel unless it has a certain shape and is of a definite size; if it is larger it is a hogshead; if smaller, a keg.

**Changes.**—Experience shows us that the properties of substances can be altered in various ways.

Every alteration constitutes a change, and for purposes of convenience, changes are arbitrarily divided into two classes, physical and chemical.

A physical change is one which alters only a very few of the properties of a substance. The moving about of a body or the heating of a piece of iron are examples of physical changes.

A chemical change is one which alters all or nearly all of the properties of a substance. In fact, after a substance has undergone a chemical change, we are unable to recognize the presence of the original substance, and in its place we find one or more new substances with different properties. The burning of wood or the rusting of iron are familiar examples of chemical changes.

From these definitions it would seem to be an easy matter to decide whether a given change is physical or chemical. And so it is in most cases. However, there are all gradations in the number of properties altered in the change, and in some cases it becomes really impossible to decide definitely to which class they belong. This is due to the fact that there is no real difference between the two changes; we have simply arbitrarily drawn a distinction as a matter of convenience in our general scheme of classification. The freezing of water is an example of a change which it is difficult to classify. So many of the

properties of ice are different from those of water that one is inclined to call freezing a chemical change, but on the other hand the transformation takes place so easily, simply upon changing the temperature, that probably the majority of people consider it a physical change.

In most cases there is no difficulty. For example, a piece of rubber when rubbed with woolen acquires the property of attracting bits of paper, but is not otherwise altered. Without question this is a physical change. If the rubber be brought in contact with a flame, it will take fire and burn with a smoky flame and continue to do so until all the rubber has disappeared. Soon after the rubber begins to burn a very strong odor will be noticed which must be due to something produced from the rubber. Since we have in this case the complete disappearance of the properties of rubber and the appearance of the properties of a new substance, this is a chemical change.

**Natural Laws.**—Having discussed the properties of substances and the changes which they undergo, we may now turn to the natural laws which describe these changes.

Experience tells us that under like conditions events repeat themselves in a very large measure, and that the more nearly the conditions are reproduced the more closely are the events duplicated. So generally is this the result of our experience that we finally become convinced that if it were possible to reproduce the conditions exactly, the events would be exactly duplicated. As a result then of our experience we are able to say, after repeated trials, just what takes place under certain conditions. Such a statement is a law of nature. A law of nature differs then essentially from a law of man in that it is simply a statement of what does happen and has in it no element of compulsion. [Man is so insignificant a part of nature that he cannot presume to dictate to her but can only observe, and learn to make the condition such that the operations of nature shall be as favorable to himself as possible.] A law of nature is a statement of the way nature works and should be so worded that it describes as large a number as possible of single phenomena and gives us the maximum amount of information concerning each.

As an illustration of a law of nature, we may select the law of falling bodies. We know as a matter of common experience

that heavy bodies if unsupported fall to the earth, and a statement to this effect is a law of nature. It would be much more useful if it gave us the results of our experience as to the velocity of the bodies after falling for given times and in addition the space passed over during certain times of fall. The law might then be worded as follows: *All heavy bodies fall toward the earth with a velocity which is equal to the force of gravity times the time that the body has been falling and the space passed over is equal to one-half the force of gravity times the square of the time of fall.*

Obviously from what has been said the wider our knowledge of the laws of nature the better equipped we are for life. They are all directly or indirectly the results of experience and their formulation is one of the most important works of science.

**The Fundamental Law of Chemistry.**—We find upon examining the properties of different bodies composed of the same substance that they agree exactly in all their essential properties, that is, the properties other than those of shape and size. We find too that other substances have radically different properties and that the change from one to another is sudden, leaving gaps which are not filled in by gradual alterations in the properties. We have then as many absolutely distinct sets of unvarying properties as there are substances.

*Bodies may be arranged in classes such that the different members of each class agree exactly with each other in all their essential properties.* The different members of each class are the bodies composed of the same substance. The law just given is known as the law of the definiteness of properties and is often called the fundamental law of chemistry.

**Properties of a Substance and the Substance.**—We have defined properties as the signs through which objects manifest themselves to us and have spoken of them as though they belonged to substances, and of the substances as though they in some way possessed the properties. Indeed the original meanings of the words would convey these ideas, and it is very hard to get away from them. However, when we come to consider just what there is about a substance which is not a property of that substance and which might be that which possesses the properties we are completely at a loss. Everything that we know about

a substance is a property of that substance and if by experimentation we find out anything more, that will also be a property; farther than this it seems to be impossible for us to conceive of anything concerning a substance that is not a property of that substance. One can be readily convinced of this by trying to think of anything about a familiar substance that is not a property of that substance. A realization of this fact does not make our conceptions of the substance any the less definite because these properties are the real things about the substance, which we can know and measure. In fact our idea of the substance is simply the sum of all these properties which we know. For us then a substance is simply *a specific group of essential properties which always occur together and to an unvarying degree under given conditions*. This may be used as a working definition of a substance. If there is anything more to a substance than its properties we can know nothing of it. We cannot even imagine anything about it. So we will leave the question of the actual existence of a possessor of properties to speculative philosophy, and in matter of fact chemistry when we say substance we will mean properties.

Every known substance has a name which in a way stands for the properties of the substance. These names can mean to us only as much as we know of the properties of the substances. So in studying chemistry we must take care that we do not merely learn the names of the various substances with which we deal, but also that we make these names mean something to us by learning the more important properties of the substances.

**Physical and Chemical Properties.**—It is convenient to divide properties into two classes—physical and chemical. A physical property is one which can be detected and measured without causing the substance to undergo more than a physical change. As examples we might give color, density, conductivity for heat or electricity, etc.

A chemical property is one which is only revealed when the substance is transformed into something else and consequently undergoes a chemical change. One of the properties of sulfur is that it burns with a pale blue flame, and finally all disappears, leaving behind something which is invisible but which has a very strong smell. Since this property is shown only when the sulfur

is transformed into a new substance, this is, therefore, a chemical property.

Since there is no real difference between physical and chemical changes, there is none between the two sets of properties, but nevertheless, it is convenient to make the arbitrary distinction.

**Identification of Substances.**—The chemist is very often confronted with the problem of deciding as to whether two different bodies are composed of the same or of different substances. The decision rests upon the answer to the question, Do the bodies have exactly the same essential properties? If they do, they are composed of the same substance; if they do not, of different substances. Evidently the question can only be answered after carefully investigating the properties. To be perfectly sure, it would seem to be necessary to compare all of the properties because two substances might agree in most of their properties and yet differ enough in some to make them different substances. The labor required for the comparison of all of the essential properties is so great that it is never done. The chemist compares some of the essential properties, and if these agree exactly he decides that the two bodies are composed of the same substance. In doing this he takes advantage of a law which states that if two bodies agree exactly in some few of their essential properties they will agree exactly in all and are composed of the same substance.

**The Characterization of a Substance.**—The properties chosen for investigation in order to characterize a substance vary with the case, but naturally they are, in general, those which can be most readily observed and measured, or else they are the ones in which the substance differs most from other substances.

The impressions produced upon our sense of sight, taste, and smell can be very easily determined, and are but rarely omitted. The physical state (solid, liquid, or gaseous) of the substance at ordinary temperature and pressure and the conditions under which it changes from one state to another are easily determined and important properties. The solubility of a substance in water is another valuable characteristic. A few words concerning some of these frequently studied properties would seem to be in order here.

**Physical States.**—We distinguish three different ways in which substances fill space and call these the physical states, giving them the names solid, liquid, and gaseous states.

**The Solid State.**—A substance is a solid if a given body composed of this substance has both a definite volume and a definite shape of its own independent of its surroundings.

**The Liquid State.**—A substance is a liquid if a given body composed of this substance has a definite volume but takes its shape from its surroundings. A liquid always runs down to the lower part of the vessel in which it is placed and takes on the shape of the vessel in so far as it can fill the container. The free surface of a liquid tends to be flat and parallel to the surface of the earth unless the body of the liquid is small, when the surface is rounded. If the body of liquid be very small and the surface entirely free, the liquid takes on the form of a sphere modified more or less by the action of gravity.

**The Gaseous State.**—The gaseous state is characterized by the fact that a gaseous substance has neither definite volume nor shape, but always fills the container in which it is placed and consequently takes its shape and volume from the surroundings.

It is a very easy matter to tell, in the great majority of cases, whether a given substance is solid or gaseous. There are, however, a few substances which are like wax in that they keep a fairly definite shape for some time and so give the impression that they are solids. If left for a longer time they slowly change their shape and flow, thus showing that they are really viscous liquids. But such substances are comparatively rare and give but little trouble in classification.

The physical state of a substance may vary with the conditions such as temperature, etc. With rising temperature, solids always tend to become either liquid or gaseous, and liquids to become gaseous. With falling temperatures gaseous substances always tend to become either liquids or solids, and liquids to become solids.

**Solubility and Solution.**—Many substances when brought in contact with water mix with the latter in varying proportions and form a homogeneous liquid which has in a general way the properties of the water and of the other substance. Such a homogeneous mixture, *i.e.*, one in which every distinguishable

particle is exactly like every other particle in essential properties, is called a solution. The ability of a substance to form a solution is called its solubility and is an important property of the substance. A more extended discussion of solution will be given at a later point, where it will be shown among other things that solutions are not necessarily liquid but may be solid or gaseous as well.

**Mechanical Mixtures.**—Substances are often present together in such a way that they do not form a homogeneous mixture but the different parts may be distinguished and more or less easily separated. Such mixtures are called mechanical mixtures. Muddy water may be given as an example of such a mixture. Examine it with a lens and the particles of silt can be seen. Allow it to stand or pass it through a filter and the silt may be separated from the water. Muddy water is not homogeneous and hence is not a solution. Solutions stand between mechanical mixtures and a very important class of substances, with which we will become familiar in a little time, known as chemical compounds.

## CHAPTER II

### UNITS

**Units.**—Some of the properties of substances, as for example color, can be ascertained by simple inspection, while others require more or less elaborate experiments to bring them to light. The constant aim is to represent these properties by numbers. To do this a unit must be decided upon and the property carefully measured in terms of this unit. Almost all of the units used in scientific work are derived directly or indirectly from three fundamental units, the centimeter, the gram, and the second, and the whole scheme of units is called the C. G. S. system. The second is the unit of time. It is in use in daily life and is familiar to everyone.

**Length.**—The centimeter is the unit of length and is the one-hundredth part of the length of a certain bar of platinum carefully preserved in Paris, which is called the "Standard Meter." This standard meter was intended to be the  $\frac{1}{10,000,000}$  of the earth's quadrant or quarter circumference, measured on the meridian of Paris, but afterward turned out to be something different from this owing to an error in the measurement. An inch is equal to a little more than 2.5 cm.

**Mass.**—The gram is the unit of mass. It is the  $\frac{1}{1,000}$  part of the mass of a certain piece of platinum called the standard kilogram. It was intended that the gram should be the mass of a cubic centimeter of water at its temperature of maximum density,  $4^{\circ}\text{C}.$ , but actually the mass of the latter is 0.999982 gm. This differs so slightly from unity that the mass of 1 c.c. of water at  $4^{\circ}\text{C}.$  is usually taken as exactly 1 gm.

**Weight.**—A heavy body is always pulled toward the earth with a certain force. This force is called its weight and is proportional to the mass of the body. The weight of a given body varies with its position on the earth, but an average is 981 dynes for each gram of the body's mass. A dyne is that force

which acting on 1 gram for 1 second will generate a velocity of 1 cm. per second.

If one takes as the unit of weight, not the dyne, but, as is commonly done the weight of 1 grm., then the numerical value of the weight of a body in terms of this unit is the same as the mass of that body. The statement that a body has a weight of 10 grm. means that its weight is the same as that of 10 grm., 9,810 dynes say, and consequently the mass is 10 grm.

**Volume.**—The unit of volume is the cubic centimeter or the still larger unit, the liter which is 1,000 c.c.

**Energy.**—Work is usually defined as the product of a force and the distance through which it acts: energy as work or the ability to do work. It has been further shown that there are many forms of energy such as heat, light, electrical energy, chemical energy, etc., and that these forms may be changed one into another without loss. In fact *in an isolated system of bodies, energy can be neither created nor destroyed, but remains present in unchanged amount.* This is the law of the conservation of energy.

The unit of energy is the erg, and this is the work done by a force of 1 dyne acting through a distance of 1 cm. This unit is rather small, and so we have the larger units, the joule, which is 10,000,000 ergs, and the kilojoule which is 1,000 joules.

Whenever work is done upon a body, the latter acquires the ability to do work, and hence an increase in energy. The simplest way to regard this change of work into energy is to consider work as one of the forms of energy. If this is done *energy may be defined as work and everything else which may be obtained from work and reconverted into work.*

**Conservation of Weight and of Mass.**—One of the most useful instruments to the chemist is the balance. This is a device by means of which the weights of bodies may be compared, and since the weights are proportional to the mass, the relative masses may be determined.

If we ask the question, how are the masses of substances affected when they undergo chemical change, we can obtain the answer by weighing the reacting substances before and after the change. We will find that in many cases there are apparent losses in weight, as in the case of burning a piece of wood and in other cases a gain in weight, as in the rusting of iron. But these

changes take place in contact with air and hence the changes in weight may be due to something escaping to the air in the case of the wood, or coming in from the air in the case of the iron.

This possible source of change in weight may be excluded by sealing the whole reacting substance air-tight in a flask. When this is done, it will be found that whatever changes in weight may be observed will be inside the limits of experimental error, for all but the most refined experiments, and even in these cases the small changes observed may perhaps be due to some source of error as yet unknown.

Neither is there any known physical change which will alter the weight at any given spot of the substance undergoing the transformation and therefore we at once set up the law of the conservation of weight which is, that *neither a physical nor a chemical change alters the total weight of the system undergoing change.*

Since mass is proportional to weight we may get from the above the law of the conservation of mass. *The total mass of a system is the same before and after any chemical or physical change which may take place within the system.* This simply means that although chemical changes alter so radically the other properties of substances they do not change that property called mass.

**Density.**—The density of a substance may be defined as the ratio of the mass of a given body composed of that substance to the volume of the body. It is expressed in terms of grams per cubic centimeter.

**Specific Gravity.**—The specific gravity of a substance is the ratio of the weights of equal volumes of that substance and of some other substance taken as a standard. Water is usually taken as the standard. The temperature of both substances must be stated in order that specific gravity may be definite. If water at 4°C. is taken as the standard substance, since at that temperature its density is one, the numerical value of the specific gravity will be the same as that of the density, although the conceptions are entirely different.

## CHAPTER III

### OXYGEN

**Discovery of Oxygen.**—Oxygen was discovered August 1, 1774, by the English chemist Priestly who prepared it by heating mercuric oxide. It was independently discovered something like a year earlier than by Priestly, by the Swedish chemist Scheele, but his results were not published until 1777. Scheele obtained

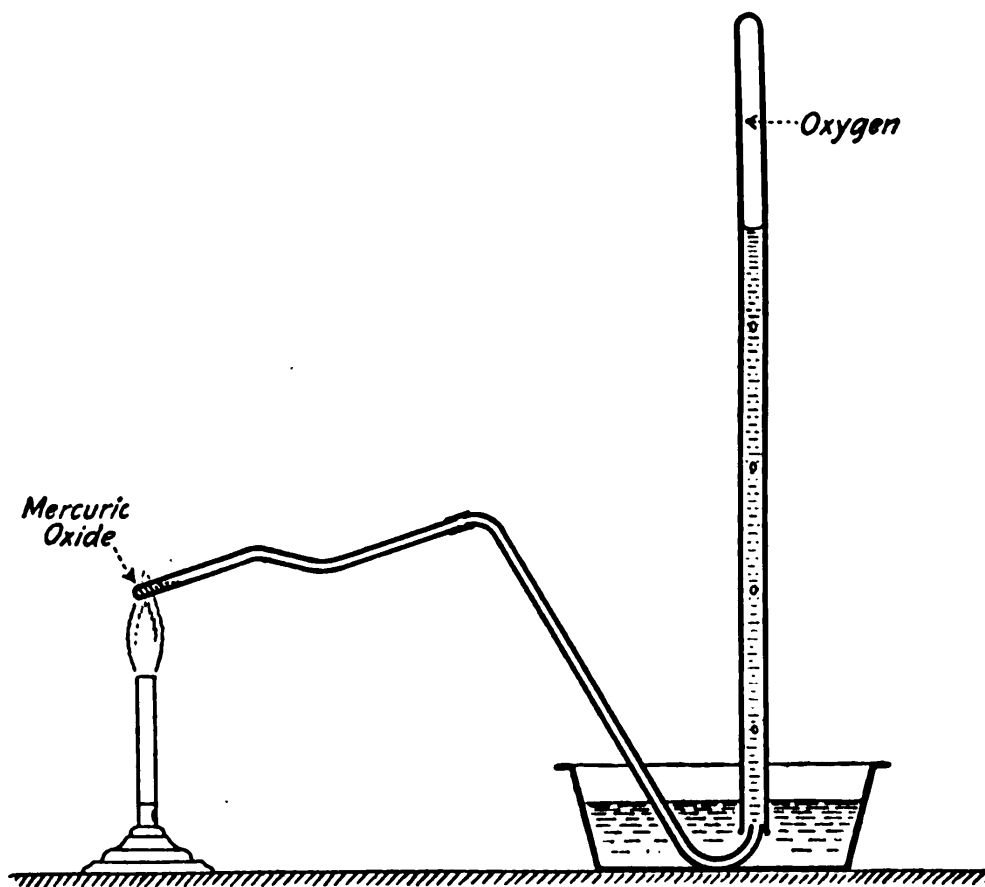


FIG. 1.

it by heating saltpeter, mercuric oxide, manganese dioxide, and a number of other substances.

Priestly's original experiment, in a somewhat modified form, may be easily repeated. Mercuric oxide, which is a reddish powdery substance, is placed in a doubly bent tube (Fig. 1) which

must be of hard glass. It is then strongly heated, and soon the mercuric oxide darkens in color and becomes almost black. If the heating be continued a bright metallic film appears on the cooler part of the tube, and at the same time, if the end of the delivery tube be placed under water, bubbles of gas will be seen to rise through the water. This gas may be collected by filling a vessel with water and placing it mouth downward in a trough of water. Upon bringing the mouth of the vessel over the delivery tube, the bubbles of gas will pass up into the vessel and gradually displace the water. When the vessel is full of the gas it may be removed from the water and placed mouth upward on the table for experimentation, taking care to keep it covered with a glass plate. It will be as transparent as air and in fact will appear just like air. It may, however, be distinguished from air by its action toward a feebly glowing spark on the end of a splinter. In oxygen the spark bursts into flame, while in air it barely continues to glow.

If the process of heating the mercuric oxide be continued, the oxide will be seen to diminish gradually in quantity and the bright metallic film to increase, and all the while the gas—oxygen—will be given off. This will go on until the mercuric oxide has all disappeared, then the process comes to an end. If the bright metallic film be examined it will be found to consist of drops of mercury, which is often called quicksilver. So we have the one substance, mercuric oxide, decomposing into two substances, oxygen and mercury which have entirely different properties from the mercuric oxide; therefore, this is a chemical change.

**Combustion.**—Experience from infancy has made us familiar with that most important set of chemical phenomena called combustion. We see the coal or wood burn in the stove, the oil or gas in the lamps. We know that a great amount of heat is universally given off during such a process. In most of the above-mentioned cases, it is very apparent that the burning substance decreases in weight. There are, however, other cases which we would certainly classify as combustion in which the weight is increased during the process of burning. For example, if a piece of metallic magnesium, in the form of a ribbon, be held in the flame of a match it will take fire and burn with an exceedingly bright light. The metal disappears and in its place is left a white powdery sub-

stance which weighs two-thirds more than the metal did before burning. Finely divided iron will burn when brought into a flame, forming a black brittle substance which weighs more than the original iron. In these and other instances of the same kind which might be mentioned, the products of combustion are solids, and hence easily obtained in a weighable form. This suggests that perhaps in every case of combustion the products are really heavier than the combustible substance, and that in the case of the wood, etc., first mentioned, the products are gaseous and hence escape our observation. That this is so may be easily shown in the case of a lamp by holding a cold object over the burning lamp when it at once becomes covered with a film of liquid water. Since this water will not accumulate if the lamp is not lighted, we conclude that the water is one of the products of the combustion of the oil. If a drop of lime water, on the end of a glass rod or a loop of wire, be brought over the flame of a lamp it will quickly become clouded. Now water vapor will not produce this cloud in the lime water nor will it appear unless the lamp is burning, and therefore we conclude that something besides water is formed during the burning of the oil. One of the characteristic properties of carbon dioxide is its ability to cloud lime water, and we then conclude that carbon dioxide as well as water is formed during the combustion of the oil. Processes by which the presence of certain substances may be detected are called tests or reactions, and the substances used, such as the lime water in this case, are called reagents. By applying these same tests to burning coal, wood or gas, it will be found that in these cases also, carbon dioxide and water vapor are formed. If the coal is anthracite, comparatively little water vapor and much carbon dioxide will be produced.

There is a solid white substance called caustic potash which has the power to take up both water vapor and carbon dioxide, and to hold them in such a form that they may be weighed.

If a glass cylinder loosely filled with this substance be placed over an unlighted candle and the whole counterpoised upon a balance and the candle then lighted (Fig. 2), the caustic potash will absorb the water vapor and carbon dioxide produced during the burning, and it will be very quickly seen that the weight of the whole is increasing, although the candle is visibly becoming

smaller. In some such a way as this it may be shown that the weight of the products of combustion is always greater than that of the combustible substance. Since in every case the products of combustion have different properties from the original substance, the changes that take place are chemical changes.

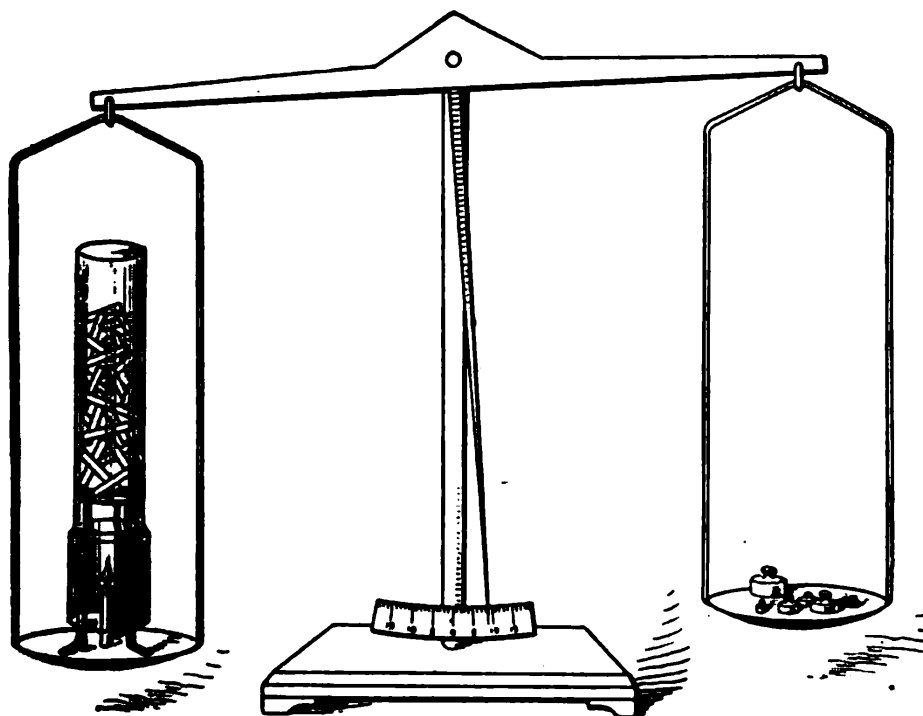


FIG. 2.

The law of the conservation of weight states that the weight of the products of a chemical change is the same as that of the substances before the change. We must conclude then that there is some other substance than that which burned taking part in the chemical change which we call combustion, and that the weight of this other substance is equal to the difference in weight between that of the products of combustion and the combustible substance.

**Rôle of the Air.**—All these changes which we have been considering take place in contact with the air, so it is very probable that this other substance is present in the air. This is confirmed by the fact that it is impossible to make a combustible substance burn in a vacuum, and further, when it burns in a limited amount of air a part of the air is used up, or disappears, but never more than one-fifth of the total volume of the air. After one kind of combustion has used up one-fifth of the air, no

other substance will burn in the remaining four-fifths. This indicates clearly that the air consists of at least two gaseous substances, one present to the extent of one-fifth of the total volume; and taking a most important part in the phenomenon of combustion.

If mercury be heated for a number of days to a temperature a little below its boiling-point in contact with a limited volume of air, a reddish substance, mercuric oxide, is formed on the

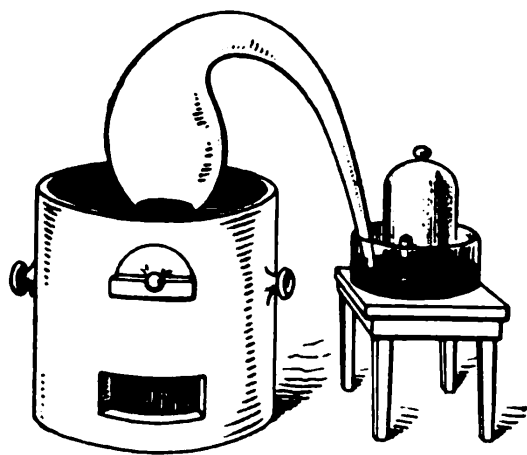


FIG. 3.

mercury, and the air gradually decreases in volume. If the mercuric oxide obtained in this way be heated as described on p. 12, it yields mercury and oxygen, and the volume of oxygen so produced is just equal to the decrease in the volume of the air. This oxygen has the power of supporting combustion to an extraordinary degree and in the burning, all the oxy-

gen may be used up. The residual air will not support combustion, but if the oxygen obtained by decomposing the mercuric oxide be added to it, the air regains all its original properties.

These experiments were first performed by the French chemist Lavoisier shortly after the discovery of oxygen, and had much to do with our present conception of combustion. The apparatus which he used is shown in Fig. 3.

**Combination and Decomposition.**—We have seen above that mercuric oxide may be transformed into mercury and oxygen. This process is an example of what is called decomposition, and the reversed process, the formation of the mercuric oxide from oxygen and mercury, is an example of combination. Processes like these compose a large part of the changes studied in chemistry.

**Preparation of Oxygen.**—Although free oxygen is present in the air in such enormous quantities, the problem of separating it from the substances with which it is mixed is by no means simple. (See liquid air, pp. 25 and 200.)

There are many other substances besides those already given which will yield oxygen upon being heated. Among these may

be mentioned potassium chlorate and potassium permanganate, and in addition oxygen may be obtained by the decomposition of water by the electric current and by acting upon sodium peroxide with water or dilute acid. The method most in use in the laboratory is that of heating potassium chlorate. This is a white crystalline substance which melts at about  $360^{\circ}\text{C}$ . and decomposes at a higher temperature into oxygen and potassium chloride. The rate of decomposition increases rapidly as the temperature is raised. Curiously enough if it be mixed with

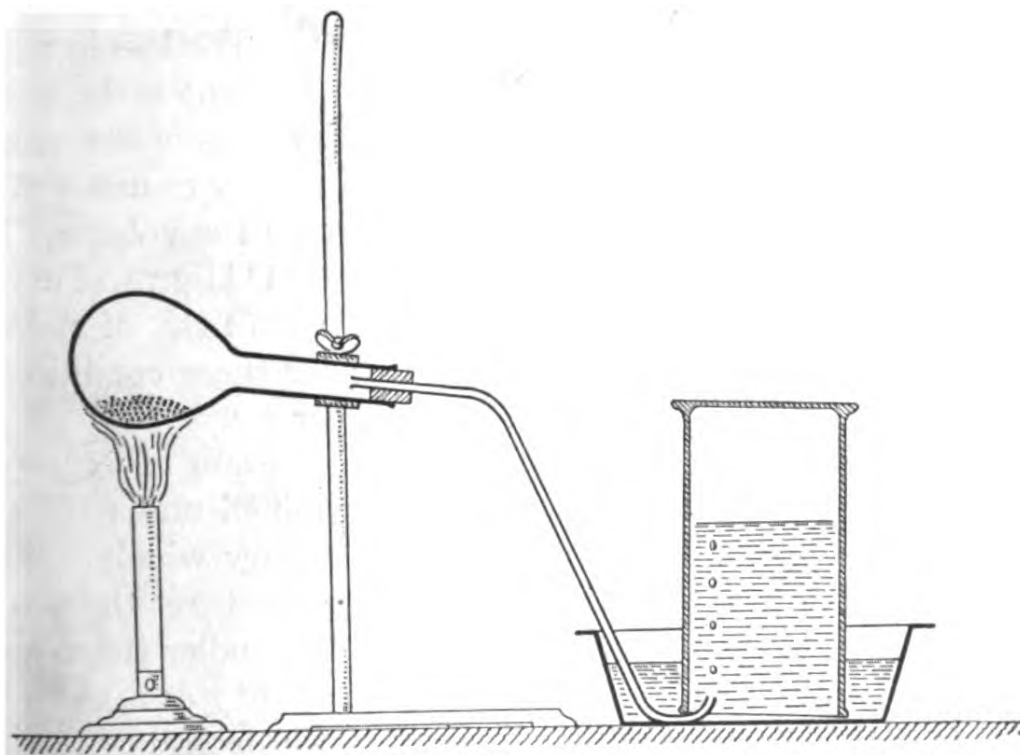


FIG. 4.

something like one-third its weight of manganese dioxide the decomposition takes place much more rapidly than with the potassium chlorate alone, being quite active at as low a temperature as  $200^{\circ}\text{C}$ ., and after the operation the manganese dioxide is found to be unaltered except, perhaps, that the particles may be a little finer than before. Although manganese dioxide will yield oxygen at a high temperature, it will not do so in noticeable quantity at  $200^{\circ}\text{C}$ ., and its action here seems to be to greatly increase, by its mere presence, the rate at which the potassium chlorate decomposes. Actions of this kind are common and are known as catalytic actions. They will be considered more in detail later.

The decomposition of the potassium chlorate when mixed with manganese dioxide may be carried out in a hard glass flask (Fig. 4). The oxygen is collected by the displacement of water as explained above.

**Physical Properties.**—The gas so obtained is colorless, odorless, and not very soluble in water or it could not be collected over this liquid.

One of the important physical properties of every substance is its density. The simplest way to determine the density of oxygen is to decompose a known weight of either mercuric oxide or potassium chlorate and weigh the residue. The loss in weight is the weight of the oxygen. If the unit of weight is the weight of 1 gram, the loss in weight gives at once the mass of the oxygen; and to obtain its density it will only be necessary to measure the volume of the oxygen, and divide the mass by the volume. For example, 1.6000 gram of mercuric oxide gave 0.1111 gram of oxygen which measured 87.15 c.c. under a pressure of 74 cm. of mercury and at 25°C. The density of oxygen under these conditions is therefore  $0.1111/87.15 = 0.0012752$  gram. per c.c.

**Standard Conditions.**—If the volume of a gram of oxygen, or of any other gas for that matter, be determined under different atmospheric conditions it will be found to vary widely. Other things being the same, the higher the temperature, the greater the volume, and the higher the pressure the smaller the volume. It can be readily seen from this that the density of a gas is not definite unless the volume of a given mass of the gas be measured at a certain definite temperature and pressure. For the sake of uniformity it is the universal custom to take the temperature of melting ice, or 0°C., as the standard temperature since this can be so easily reproduced. As the standard pressure, is taken the mean pressure of the air at the sea level, which is equal to that of a column of mercury 76 cm. in height. Since the density of the mercury changes with the temperature, the mercury should also be at 0°C.

### THE GAS LAWS

**Boyle's.**—As it is usually not convenient to measure the volume of gases under standard conditions, it is a matter of great importance to know just how they change their volumes with

changes in pressure and temperature, so that their volumes may be read under any convenient conditions and corrected to what they would be under standard conditions. Fortunately it has been found that gases behave so nearly alike that the same corrections will do for all unless extreme accuracy is demanded.

The simplest relationship is that between the volume and the pressure, and this has been known ever since 1660, when it was discovered by the English scientist Robert Boyle.

Boyle found that if the pressure upon a fixed mass of a given gas, at constant temperature, be doubled, trebled, or quadrupled, the volume of the gas would be reduced to one-half, one-third, or one-fourth of its original volume, or in other words the volume of a fixed mass of a given gas at constant temperature is inversely proportional to the pressure. This is known as Boyle's law, and may be represented as follows:

$$v = k \frac{1}{p} \quad (1)$$

when  $v$  and  $p$  are the simultaneous values of the volume and pressure under which the gas is measured.

The above relation may also be expressed in the following form:

$$p_1 v_1 = p_2 v_2 = pv = \text{const.} \quad (2)$$

where  $p_1 v_1$  and  $p_2 v_2$  are pairs of simultaneous values of pressure and volume. In words this is expressed as follows: *The product of the simultaneous values of the pressure and the volume for a fixed mass of a gas at constant temperature is a constant.* This is simply another way of wording Boyle's law.

As an example of the practical application of this law we may take the data given above for the density of oxygen. There we had 87.15 c.c. of oxygen at 25°C. and a pressure of 74 cm. of mercury. What would be the volume at the same temperature but under the standard pressure of 76 cm. of mercury?

Taking equation (2) we have

$$p_1 v_1 = p_2 v_2$$

and letting  $p_2 = 74$ ,  $v_2 = 87.15$  c.c. and  $p_1 = 76$  cm. of mercury,

$v_1$  = volume at this standard pressure. Solving for  $v_1$  we get:

$$v_1 = \frac{p_2 v_2}{p_1}$$

$$v_1 = \frac{74 \times 87.15}{76} = 84.85 \text{ c.c.}$$

This would be the volume of the gas if measured at the temperature  $25^\circ\text{C}$ . under the standard pressure.

In order to calculate the volume which the gas would occupy at the standard temperature as well as pressure, it would be necessary to ascertain the influence of a given change in the temperature upon the volume of a fixed mass of a gas at constant pressure, and apply the proper correction to the calculated volume of the gas at the standard pressure. As indicated above, the volume of a fixed mass of gas increases with rising temperature, the pressure remaining constant. If we take the volume occupied by a certain mass of a gas at the melting-point of ice or  $0^\circ\text{C}$ . as unity, and then heat the gas to the temperature of water boiling under a pressure of 76 cm. of mercury, the volume of the gas will be found to be 1.367, so that the increase has been 0.367. If now we divide the difference in temperature between the melting-point of ice and the boiling-point of water into 100 equal parts, as has been done in the Centigrade thermometer system, the increase in volume for each degree is 0.00367 or  $\frac{1}{273}$  of the volume at  $0^\circ\text{C}$ . This is called the coefficient of expansion of the gas and is represented by alpha, " $\alpha$ ."

The law describing this behavior is called **Gay Lussac's and Dalton's Law** or sometimes **Charles' Law** and was discovered simultaneously by Gay Lussac and Dalton in 1802. It may be expressed as follows: *The volume of a fixed mass of a gas at constant pressure is increased by  $\frac{1}{273}$  of its volume at  $0^\circ$  Centigrade for each degree's rise in temperature.*

The mathematical expression is

$$v_t = (1 + \alpha t)v_0$$

where  $v_0$  = volume at  $0^\circ\text{C}$ .,  $v_t$  = the volume at the temperature  $t$ ,  $t$  = the temperature, and  $\alpha$  the coefficient of expansion, 0.00367 or  $\frac{1}{273}$ . The conditions under which this will hold are that both the mass of the gas and the pressure upon it must remain constant.

**Absolute Temperature.**—Since all gases are so regular in their behavior toward changes of temperature the change in the volume of a fixed mass of a gas under constant pressure has been taken as the measure of the change in temperature. Gas thermometers are really the standard instruments for the measurement of temperature at the present time. Mercury thermometers are used as working instruments because they are somewhat more convenient than gas thermometers.

In the Centigrade thermometer system, the melting-point of ice has been called  $0^{\circ}$  and the boiling-point of water  $100^{\circ}$ . If a fixed mass of a gas at constant pressure be raised in temperature from the melting-point of ice to the boiling-point of water (Fig. 5), its volume will be increased by  $\frac{100}{273}$  of its volume at  $0^{\circ}\text{C}$ . Since we have already decided to call the temperature interval between the freezing- and the boiling-point of water  $100^{\circ}$  and to take the change in the volume of a gas as the measure of the change in the temperature, we say that if a fixed mass of a gas at constant pressure changes its volume by  $\frac{1}{273}$  of its volume at  $0^{\circ}\text{C}$ , its temperature has been changed by  $1^{\circ}\text{C}$ . If it changes its volume by  $\frac{20}{273}$  of its volume at  $0^{\circ}\text{C}$ , the change has been  $20^{\circ}$ .

It is a very simple matter to cool a gas to a temperature below  $0^{\circ}\text{C}$ . The gas contracts during the process and continues to do so as it is cooled to lower and lower temperatures. In accordance with what has been said above, we consider that the gas has been cooled  $1^{\circ}$  for each  $\frac{1}{273}$  of its volume at  $0^{\circ}\text{C}$ , which it has lost, the pressure and the mass of gas being constant. It is very obvious that a gas cannot lose more than  $\frac{273}{273}$  of its volume because this would reduce it to zero volume. Therefore, the lowest temperature to which a gas can be cooled is 273 Centigrade degrees below the Centigrade zero and this temperature is called absolute zero. As a matter of fact all gases are liquefied or solidified before they reach this temperature, and since the gas laws do not describe the

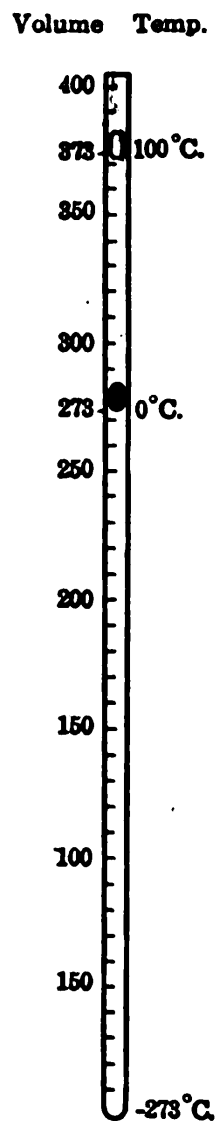


FIG. 5.

behavior of liquids or solids the substances would doubtless have some volume even if cooled to absolute zero. The lowest temperature yet reached is about  $3^{\circ}$  above absolute zero which is the temperature at which liquid helium will boil under diminished pressure.

Temperatures reckoned upward from this absolute zero are called absolute temperatures. The absolute temperature of melting ice is  $273^{\circ}\text{A.}$ , and of boiling water  $373^{\circ}\text{A.}$  Temperatures on the Centigrade scale may be readily changed to the absolute scale by adding 273 to the Centigrade temperature. Absolute temperatures are usually represented by  $T$  and Centigrade by  $t$ , so,

$$T = t + 273$$

There are two important advantages of the absolute over the Centigrade system. First, by its use one does away with all negative temperatures and second, we are enabled to state the law of Gay Lussac and Dalton in the following exceedingly simple manner. *The volume of a fixed mass of a gas at constant pressure is directly proportional to the absolute temperature.* In symbols this law is expressed as follows:

$$v = k'T \tag{3}$$

where  $v$  is the volume,  $k'$  the proportionality factor, and  $T$  the absolute temperature.

By a simple transformation of equation (3) we get

$$\frac{V}{T} = k'$$

or the volume of a fixed mass of a given gas divided by the absolute temperature at which it is measured is equal to a constant. From this it follows that

$$\frac{V_0}{T_0} = \frac{V_1}{T_1} \tag{4}$$

in which  $V_0$ ,  $T_0$  and  $V_1$ ,  $T_1$ , are any different sets of simultaneous values of the volume and temperature for the same sample of gas.

With the aid of equation (4), we may readily calculate the volume of a given sample of gas at one temperature from its

volume at another provided the pressure remains constant. This may be illustrated by calculating the volume of the oxygen obtained on p. 18 at the standard temperature of 0°C. or 273°A. On p. 20 we made the correction for pressure according to Boyles' law and found that at 25°C. or 298°A. and under the standard pressure, the volume would be 84.85 c.c. Letting  $V_0$  be the volume at 273°A.,  $V_1$  be 84.85 and  $T_1$  be 298°A., we get

$$\frac{V_0}{273} = \frac{84.85}{298}$$

or

$$V_0 = 84.85 \times \frac{273}{298} = 77.74 \text{ c.c.}$$

To obtain the density of oxygen under standard conditions all that remains to be done is to divide the mass of the oxygen, 0.1111 grm. by this calculated volume, 77.74 c.c.

$$\text{Density} = \frac{0.1111}{77.74} = 0.0014293 \text{ grm. per c.c.}$$

**The Combined Gas Laws.**—In calculating the volume of the oxygen obtained on p. 18 we first corrected for pressure by multiplying the measured volume 87.15 c.c. by the ratio of the measured pressure 74 cm. to the standard pressure 76 cm. and then took this result, 84.85 c.c., and corrected for temperature by multiplying it by the ratio of the standard temperature, 273°A. to that at which the gas was measured 25°C. or 298°A. Obviously these operations might just as well have been combined and the double correction made at once, as follows:

$$V_0 = 87.15 \times \frac{74}{76} \times \frac{273}{298} = 77.74 \text{ c.c. at } 0^\circ\text{C. and } 76 \text{ cm.}$$

of mercury.

This is a perfectly general relationship and may be represented by

$$V_0 = V_1 \times \frac{P_1}{P_0} \times \frac{T_0}{T_1} \quad (5)$$

We may then calculate the volume of any given sample of gas at any desired condition of temperature and of pressure from its volume at any other temperature and pressure by multiplying the given volume first by the ratio of the pressures and second by the ratio of the absolute temperatures. In

applying this relation it is, of course, necessary to get the proper temperature and pressure in the numerator. To do this, it is merely necessary for the calculator to ask himself, "Will the given change in pressure increase the volume?" If so, the larger pressure is put in the numerator; if not, in the denominator; and correspondingly for the temperature. The use of absolute temperatures is advised but may be avoided in the correction to standard conditions by using the following equation which is easily derived from equation (5)

$$V_0 = \frac{V_1 P_1}{76(1 + 0.00367t)}$$

in which  $t$  is the Centigrade temperature at which the volume  $V_1$  is measured.

**Other Physical Properties of Oxygen.**—Solubility is one of the very important properties of a substance, a knowledge of which goes to make up our conception of the substance. As has been pointed out above, oxygen is not very soluble in water or it could not have been collected over this liquid. Its solubility in water, however, is easily measured since one volume of water at  $0^\circ\text{C}$ . dissolves 0.04890 volumes of oxygen. At higher temperatures the solubility is smaller. Many metals absorb noticeable quantities of oxygen. Melted silver, for example, takes up something like 10 times its own volume of oxygen, the greater part of which it gives off on cooling. The escaping gas causes protuberances of silver to grow out from the bead, and produces the phenomenon known to assayers as sprouting.

**Liquid Oxygen.**—If oxygen under atmospheric pressure be cooled below  $-182.5^\circ\text{C}$ . it becomes a pale blue liquid which has a density of 1.12 and boils under atmospheric pressure at  $-182.5^\circ\text{C}$ . If the pressure be lowered the boiling-point falls until under a pressure of 0.75 cm. of mercury the liquid boils at  $-211.2^\circ\text{C}$ . Upon raising the pressure the boiling-point rises, and finally under a pressure of 50.8 atmospheres the boiling-point is  $-118.5^\circ\text{C}$ . If the temperature be raised any higher than this the oxygen refuses to remain in or take on the liquid state no matter how great the pressure. Hence to liquefy oxygen it must be cooled to at least  $-118.5^\circ\text{C}$ ., then upon the application of sufficient pressure, which at  $-118.5^\circ\text{C}$ . is 50.8 atmospheres

but is lower if the temperature is lower, the liquid appears. At ordinary temperatures or at any temperature higher than  $-118.5^{\circ}\text{C}$ . it is not possible to liquefy oxygen by any pressure however great.

All other gases behave as oxygen does in this respect. Each gas has a certain temperature above which it is impossible to liquefy it. This temperature is called the **critical temperature**, and the pressure which will be just great enough to bring about the liquefaction at the critical temperature is called the **critical pressure**. In the case of oxygen, the critical temperature is  $-118.5^{\circ}\text{C}$ . and the critical pressure is 50.8 atmospheres. An atmosphere is a pressure equal to 76 cm. of mercury. For other gases, the critical constants are different, and are characteristic for each substance. In learning the properties of any given gaseous substance, a fairly definite notion of its critical constants and boiling-point should be obtained.

Air is a mixture of approximately one part by volume of oxygen and four parts by volume of other gaseous substances, chiefly nitrogen. Liquid air has something like the same composition but is a little richer in oxygen because this is more easily liquefied than the nitrogen. If the liquid air be allowed to boil away, the nitrogen will come off in relatively greater quantities than the oxygen and the liquid will gradually become richer and richer in oxygen, and finally will yield a gas containing 95 per cent. or more of oxygen. This is the basis of the most important method for the preparation of oxygen upon a commercial scale. The gas is put upon the market in strong steel cylinders under a pressure of 100 atmospheres.

Both gaseous and liquid oxygen are attracted by a magnet although the attracting force is very much smaller than that exerted upon an equal weight of iron.

**Solid Oxygen.**—When oxygen is cooled with liquid hydrogen, it freezes to a light blue solid which melts at  $-227^{\circ}\text{C}$ .

**Chemical Properties.**—The ability to support combustion to an extraordinary degree is the chief chemical property of oxygen, and is made use of in its identification by introducing into some of the gas a glowing spark on the end of a stick, when it at once bursts into flame. This is the test or reaction for oxygen and the splinter or spark is the reagent.

There are two good reasons why the wood burns faster in the oxygen than in the air. The first is that since air is only one-fifth oxygen, more oxygen is in contact with the wood at a given time in the pure gas than in air, and naturally they combine more rapidly. Second, in the case of the combustion in the air, the heat given out in the burning of the wood is divided between the wood, the oxygen, the rest of the air and the products of combustion; and so of course the temperature cannot rise as high as in the case of the combustion in pure oxygen, where it has only the wood, the oxygen, and the products of combustion to warm. Now the same thing is true in this case that was mentioned about the decomposition of potassium chlorate, that the reaction goes on much faster the higher the temperature. Therefore the rapid combustion in oxygen is due to the more abundant supply of the gas and to the higher temperature.

From this explanation we would expect that other things would burn more rapidly in oxygen than in air, and upon trial we find our expectation realized. For example sulfur burns in the air with a pale blue flame of very little luminosity, while in oxygen it burns with a bright blue flame. Phosphorus burns in air with a yellowish-white flame, in oxygen the combustion is exceedingly rapid and the light is so intense as to be fairly dazzling.

Many substances which will not readily burn in the air will do so in oxygen, for example iron. If a piece of iron be heated in the air, it becomes covered over with a coating of something which may be separated rather easily from the iron, and at the same time that the coating is formed the iron increases in weight. If a thin piece of iron, say a watch spring, be heated white hot in oxygen it will take fire and burn vigorously, throwing off sparks in a very spectacular manner. The substance left after the combustion is the same as that formed by heating the iron in the air.

We know as a matter of practical experience that in order to make things burn rapidly it is necessary to raise their temperature, and therefore it might seem natural to ask what the **kindling temperature** is in each case. Experiment will tell us that combustible substances combine with oxygen at temperatures far below that at which they burst into flame; that with rising temperature the rate at which the combination or combustion

takes place increases very rapidly until finally the substance kindles into flame. It is not possible to locate very accurately this temperature at which kindling into flame takes place as it depends upon many factors, such as the state of subdivision of the substance, etc. Still less is it possible to locate a temperature above which a substance will combine with oxygen, while below it the reaction will not take place. The rate simply becomes smaller and smaller as the temperature falls. We therefore must conclude that all combustible substances combine with oxygen at all temperatures, although the rate may be immeasurably small.

The combination of oxygen with a combustible substance at temperatures below the kindling point is called **slow oxidation**. This is not essentially different from combustion, and with rising temperature gradually merges into the latter. As much heat is given off during slow oxidation as during the rapid combustion of the same quantity of the substance. If this heat is retained and goes to raise the temperature of the body, as for example, when the reaction takes place in the midst of a heap of coal, the temperature may rise high enough for the substance to burst into flame. When this happens we say it is a case of spontaneous combustion.

**Quantitative Relations.**—If we study with care the decomposition of mercuric oxide, taking into account the weights of the various substances, we will find that the weight of the oxygen formed plus that of the mercury is just equal to the weight of the mercuric oxide taken. This shows, of course, that nothing else than mercury and oxygen is formed from mercuric oxide. We will find too that, no matter how or where the mercuric oxide is prepared, there will always be a constant ratio between the weight of the mercury and the weight of the oxygen obtained by decomposing mercuric oxide. This ratio is also the same as that in which the mercury and oxygen combine to form mercuric oxide.

This is simply one example of the law of constant or definite proportions, which is one of the most important of the laws of chemistry, and may be stated as follows: "*Whenever two or more substances combine to form another substance, they do so in a perfectly fixed and invariable ratio by weight.*" \*

**Elements.**—As we have seen above, mercuric oxide yields two substances, oxygen and mercury, whose combined weights are equal to that of the mercuric oxide, while their individual weights are less. This was spoken of as decomposition, and it is a common characteristic of all decomposition processes that substances are produced whose individual weights are less than the weight of the substance from which they were formed. If we examine the chemical transformations which oxygen undergoes, we will find that in no case is there a substance formed whose weight is less than that of the oxygen used up. In one case, that of the formation of ozone (p. 29), the weight of the resulting substance is the same as that of the oxygen consumed; in all other cases it is greater. We must conclude then that oxygen has never been decomposed, that is, changed into something having a smaller weight. The same is true for mercury, and for about 80 other substances. *These substances are called the elements,<sup>1</sup> and in all ordinary chemical transformations they yield substances of either equal or greater, but never less weight than their own.*

Many of these elements are familiar from our contact with them in every-day life; for example, oxygen, mercury, sulfur, iron, copper, lead, gold, silver, carbon, tin and zinc. A complete table of the elements may be found on p. 79.

**Compounds.**—These elements are capable of entering into combination with one another, thus giving rise to the almost innumerable substances known to chemists as chemical compounds. These chemical compounds show the following characteristics. They have entirely different properties from those of the elements from which they are formed. They are homogeneous. The proportions by weight in which the elements combine is in accord with the law of constant proportions. The weight of the compound is always greater than that of any one of the elements from which it was formed and is equal to the sum of their weights. Probably the most important of all properties is that described by what is known as the *law of the conservation of the elements*. *No ordinary chemical process (ex-*

<sup>1</sup> The word "ordinary" is introduced here to exclude radio-active transformation, since it is possible that in these cases the above statement may not hold.

*cluding radio-active changes) ever produces from a compound any other elements than those which united for its formation, and these elements are reproduced in precisely the proportion by weight in which they combined for the formation of the compound.* These points may be illustrated by mercuric oxide. It may be formed by the union of the two elements oxygen and mercury in definite proportion by weight. Its properties are very different from those of mercury and of oxygen, and no elements but mercury and oxygen have been obtained from it. With a proper understanding of the meaning of the term "element," we may now resume the discussion of the element oxygen.

**Occurrence in Nature.**—As we have already seen, oxygen makes up about one-fifth of the volume of the air. That the air is a mixture of gases and not a chemical compound will be shown later. An element which is found in nature uncombined chemically with any other elements, although it may be mixed with them, is said to exist in the "free state." Since there is such a great quantity of air, oxygen in the free state is very plentiful. The compounds of oxygen are numerous and exceedingly abundant. More than 47 per cent. of the earth's crust and eight-ninths of the water is oxygen.

Almost every one of the elements is capable of undergoing chemical change with oxygen. Each substance so formed differs radically in its properties from either oxygen or the other element. Its weight is equal to the sum of the weights of the other element and of the oxygen, and the two elements unite for the formation of the substance in perfectly definite proportion by weight. Therefore all substances formed in this way are chemical compounds, and since they all have one common component, oxygen, they are called oxides. We have, for example, oxide of mercury, oxide of iron, oxide of lead, etc.

**Preparation of Ozone.**—When oxygen is exposed to the influence of the silent electrical discharge, (Fig. 6) it undergoes remarkable alterations in its properties, and is partially transformed into a new substance called ozone. By removing the latter as it is formed, the whole of the oxygen can be changed into ozone.

**Physical Properties of Ozone.**—When oxygen is converted into ozone, the volume of the ozone is only two-thirds that of the

oxygen from which it was formed and consequently its density is one and one-half times that of oxygen or 0.002144. It boils at  $-119^{\circ}\text{C}$ . and may be obtained as a deep blue liquid by passing ozonized oxygen through a tube cooled with liquid air. Gaseous ozone has a faint blue color and a very strong odor. It is somewhat soluble in water.

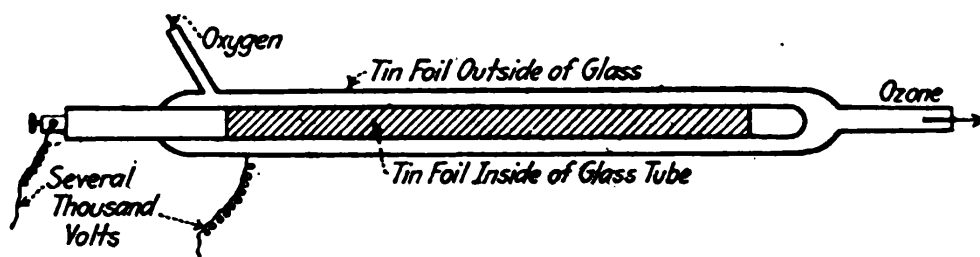


FIG. 6.

**Chemical Properties.**—Gaseous ozone has a very irritating action on the mucous membrane. A piece of bright silver when exposed for some time to ozone becomes blackened. A colorless solution of potassium iodide becomes dark brown from liberated iodine when exposed to the action of ozone although oxygen has no effect on it.

If ozone be heated to a temperature of  $250^{\circ}$  to  $300^{\circ}\text{C}$ . it is changed back to oxygen again with an increase in volume equal to the contraction which took place when the ozone was formed. The presence of metallic silver and also of several metallic oxides increases the rate at which this transformation of ozone into oxygen takes place at any given temperature. Many coloring substances are destroyed by ozone and hence it is used as a bleaching agent. It rapidly destroys the lower organisms, such as bacteria, and is therefore used as a disinfectant. In general its action is one of oxidation and differs from oxygen chiefly in that it is more vigorous and that usually one-third of the weight of ozone is used in oxidizing and two-thirds becomes ordinary oxygen. Liquid ozone is a very dangerous substance since it explodes with great violence either when brought in contact with an easily combustible substance or when its temperature has reached its boiling-point. The gas when compressed is also explosive.

**Uses for Ozone.**—As was mentioned before, ozone is used for bleaching of oils, paper, delicate fabrics, and flour, sterilization of

water, and in addition is used for the purification of air and of starch, resinification of oils, and in the aging of liquors. Its use for the purification of air is of somewhat doubtful value, since to destroy bacteria in air the ozone must be strong enough to kill guinea pigs and in this strength would in all probability be dangerous to human beings.

**Allotropy.**—Oxygen may be converted into ozone or ozone into oxygen without any alteration in weight. From this the conclusion is drawn that no other substance combines with the oxygen for the formation of the ozone. This conclusion is confirmed by the fact that when phosphorus is acted upon by ozone in one case and oxygen in another, the same substance, phosphorus pentoxide, is formed in each case, and if equal weights of oxygen and ozone are taken, the weight of phosphorus pentoxide formed in each experiment will be the same. What then is the difference between oxygen and ozone?

Whenever oxygen is transformed into ozone, energy is taken up; and when the ozone is changed back into oxygen, this energy reappears, generally in the form of heat.

Ozone then is to be regarded as a modification of the element oxygen, possessing more energy than the latter. This property which oxygen has in common with several of the other elements of existing in two or more distinct forms, each having its own set of properties, even when the physical state of the different forms is the same, is called allotropy.

Allotropy then is the property shown by certain elements of existing in more than one distinct form, each having the same physical state but possessing different properties. The different forms are spoken of as allotropic modifications of the element.

The fundamental difference between the allotropic modifications of any one element consists of a difference in energy, although in some cases, and possibly in all, there is a difference in molar weight (see p. 68).

## CHAPTER IV

### HYDROGEN

Hydrogen was shown to be a distinct substance by Cavendish in 1766. It had been observed as an inflammable gas many years before, but was confused with other inflammable gases. That it is an element is shown by the fact that whenever it undergoes chemical changes the substances produced weigh more than the hydrogen which was transformed. Like oxygen it is a gas at ordinary temperatures.

**Occurrence.**—Hydrogen occurs free in nature in rather small quantities. It is found in the gases given off from some volcanoes and fumaroles and is present in the air to the extent of something like one volume in 30,000 volumes of air. The quantity is so small that it is difficult to determine it with accuracy. In the combined state it is very abundant. Its chief compound is water, of which it forms 11.19 per cent. by weight, the remainder being oxygen. It occurs also in combination in coal, petroleum, natural gas, and in almost all substances of animal or vegetable origin. It is the essential element in a large and important class of substances known as the acids.

**Preparation of Hydrogen.**—Since water is so abundant and contains so much hydrogen it would seem natural to suppose that hydrogen might be obtained from it economically by some such process as was used in the preparation of oxygen.

The preparation of oxygen from its compounds is comparatively simple because there are several compounds, for example, mercuric oxide and potassium chlorate, which will break up on being heated to a moderate temperature into gaseous oxygen and some other substance which is either liquid (mercury) or solid (potassium chloride) at ordinary temperatures, and can consequently be readily separated from the gaseous oxygen.

In the case of hydrogen, neither water nor any other compound has these properties and, therefore, a different method of preparation is required. At a fairly high temperature, water can be

partially decomposed into hydrogen and oxygen, but there is no practical method for the mechanical separation of these two gases. However, if there were present in the heated steam something with which the oxygen in the water vapor could combine to form a compound which is either solid or liquid at ordinary temperature, it ought then to be possible to separate this compound from the hydrogen and so get the latter in the pure state.

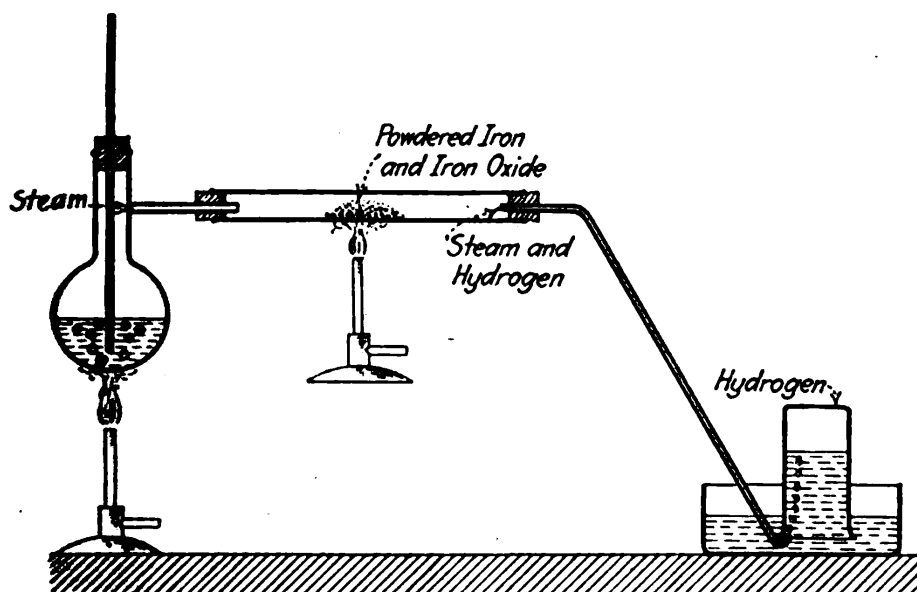


FIG. 7.

Metallic iron forms a compound with oxygen which is solid even at very high temperatures, and if steam be passed over finely divided iron, heated to redness in a tube (Fig. 7) iron oxide and hydrogen will be formed. The iron oxide will remain in the tube, while the hydrogen, mixed with much unchanged steam, will pass on over. The hydrogen may be collected by the displacement of water, as was done with oxygen, the steam which accompanies it being condensed in the water of the pneumatic trough.

The place of the iron may be taken by several other metals. Magnesium, for example, may be used, in which case the temperature may be very much lower. In fact magnesium will rapidly decompose boiling water if a little of a magnesium salt is dissolved in the water to keep the surface of the magnesium free from the magnesium compound formed.

Metallic calcium in the form of turnings decomposes cold

water at a convenient rate, thus furnishing a ready means for the preparation of hydrogen on a small scale.

The metals sodium and potassium act upon water so vigorously, even at ordinary temperatures, that only very small quantities of the metals can be brought in contact with water without giving rise to dangerous explosions. These methods consist essentially in treating the compound of hydrogen, water, with some other element which combines with the rest of the compound other than hydrogen and leaves the hydrogen free. These are examples of one of the most commonly used methods for the preparation of the elements from their compounds.

In each of these cases hydrogen and a non-gaseous substance result from the action, and the non-gaseous substance contains the metal and the oxygen. In addition it sometimes contains some hydrogen as we shall see later.

**Preparation from Acids.**—As has been stated above, hydrogen is present in all acids. As examples of acids may be men-

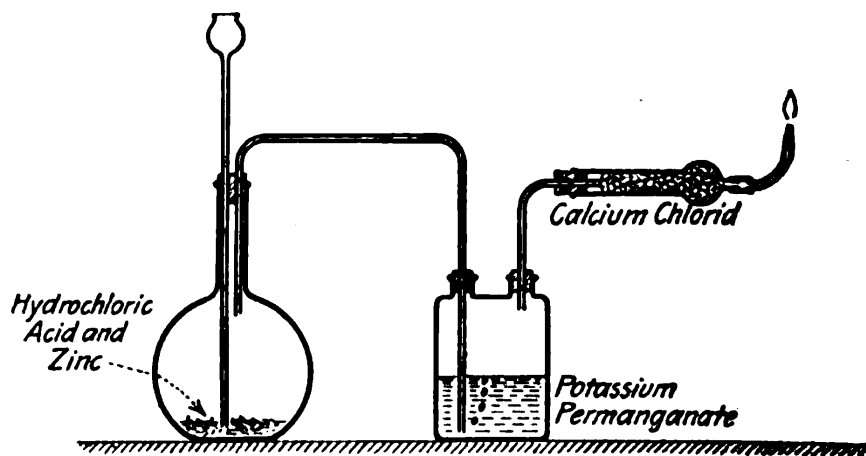


FIG. 8.

tioned sulfuric, hydrochloric, acetic acids, etc. When acids are mixed with water and brought in contact with many metals, hydrogen is given off, and each metal forms a compound with the rest of each acid. The hydrogen in each case comes from the acid and not from the water. Although most metals and acids will work in this way, in some cases the action may be violent, in others extremely slow. Metallic zinc with either dilute sulfuric or hydrochloric acid works very regularly and at a convenient rate, hence these substances are largely used in the laboratory for the preparation of hydrogen (Fig. 8).

Hydrogen is similarly prepared on a commercial scale or for filling balloons by the action of sulfuric acid on iron, but the iron always contains some carbon, and the hydrogen obtained in this manner is contaminated with compounds of hydrogen and carbon.

**Electrolytic Preparation.**—When two pieces of platinum, a metal which is very resistant to chemical action, are placed in water containing a little sulfuric acid, and connected to a suitable source of electricity, a current of electricity passes through the dilute sulfuric acid from one piece of platinum to the other. At the same time, free oxygen appears at one of the platinum plates and free hydrogen at the other. The process is really quite complex, but since the water gradually disappears and hydrogen and oxygen appear in the proportion in which they will form water, while the quantity of sulfuric acid in the solution is unaltered, it amounts to the decomposition of water at the expense of electrical energy. Here water is decomposed with the absorption of electrical energy very much as mercuric oxide is decomposed at high temperature with the absorption of heat, which it will be remembered is a form of energy. Since the hydrogen and the oxygen are given off at different points, it is an easy matter to collect each separately. One of the methods for the commercial preparation of hydrogen is based upon this principle using, however, plates of lead instead of the very expensive platinum. A solution of sodium hydroxide may be used instead of the sulfuric acid, but in this case the metal plates should be of iron or nickel.

**Purification of the Hydrogen.**—The hydrogen prepared by the methods outlined above always contains water vapor, and usually compounds of hydrogen and carbon from the carbon contained in the metal. The hydrocarbons may be largely removed by passing the gas through a solution of potassium permanganate. To remove the water vapor, advantage is taken of the fact that there are several substances which vigorously retain water while having no action upon hydrogen. One of the most convenient of these is granulated calcium chloride. This is a white, very hygroscopic substance which is formed as a waste product in many chemical operations and is therefore cheap. The calcium chloride is usually placed in a tube through which the gas is

passed. The column of calcium chloride should be as long as convenient and held in place by plugs of cotton wool (Fig. 8).

Concentrated sulfuric acid is a far more efficient drying agent than calcium chloride and is largely used. Since this is a liquid it is either placed in a suitable container and the gas bubbled through it, or it is taken up by pumice stone and packed in drying tubes or towers.

**Physical Properties.**—Hydrogen has no taste or color. The pure gas has no odor, but that prepared by the action of acids upon metals usually has a disagreeable odor due to the compounds of carbon and hydrogen which have been mentioned above. After the gas has been passed through a solution of potassium permanganate, it is so far purified that it loses the greater part if not all of the odor.

Its density is smaller than that of any other known substance, being 0.00008986 gram. per cubic centimeter under standard conditions. This is perhaps the most important physical property of hydrogen, since upon it depends its use in balloons. The density of pure dry air under standard conditions is 0.001293 gram. per cubic centimeter or 0.0012031 gram. per cubic centimeter more than the density of hydrogen, consequently 1 c.c. of hydrogen under standard conditions will have an upward flotation of 0.0012031 gram. when surrounded by air under the same conditions.

The extreme levity of hydrogen may be easily shown by filling a small rubber balloon with the gas when it will float in the air and exert a lifting power of something like a gram per liter. Or soap bubbles may be blown with the gas, and these upon being detached from the pipe will rise rapidly.

Another way to demonstrate this same property is to fill two cylinders with hydrogen and hold one of them mouth upward and the other mouth downward. After a few minutes bring a flame to the mouth of each jar. It will be found that the one with the mouth upward contains only air, while the one with the mouth downward still contains hydrogen since the gas burns.

**Diffusion.**—Because of the very great difference in density between hydrogen and air one would expect that if two cylinders were brought together mouth to mouth (Fig. 9a) the upper one filled with hydrogen and the lower one with air, that the gases

would remain unmixed. But if they are left in this position for a few hours it will be found that both cylinders contain hydrogen and air. If the cylinders are of the same size and have been left in position for a sufficient length of time, the upper cylinder will contain as much air as the lower, and the lower will contain as much hydrogen as the upper. This spontaneous mixing of one gas with another, even against the action of gravity, is an example of the phenomenon called diffusion.

All gases diffuse into one another and the process goes on until each gas is uniformly distributed through the entire space. If the pressure of each gas be measured separately, it will be found that diffusion continues until the pressure of any given gas is the same in all parts of the space; and further, it will be found that the pressure exerted by each gas is the same as that which the given mass of the gas would have exerted if it alone were occupying the entire space. This pressure is called its partial pressure. The total pressure of a gaseous mixture is the sum of all the partial pressures of its component gases. The volume of each gas is the total volume of the space occupied by the entire gaseous mixture.

The law which describes these phenomena is known as Dalton's law of partial pressures, and may be stated as follows: *Each gas, in a gaseous mixture, pervades the entire space occupied by the mixture and exerts a pressure equal to that which it would give if it were the only gas present; and the total pressure of the mixture is the sum of these partial pressures of the component gases.*

This law may be expressed in symbols by representing the total volume by  $V$ , and that of the separate gases by  $v_1, v_2, v_3, \dots$  and the total pressure by  $P$ , and the partial pressures by  $p_1, p_2, p_3, \dots$  then,

$$v_1 = v_2 = v_3 = V$$

and

$$p_1 + p_2 + p_3 = P$$

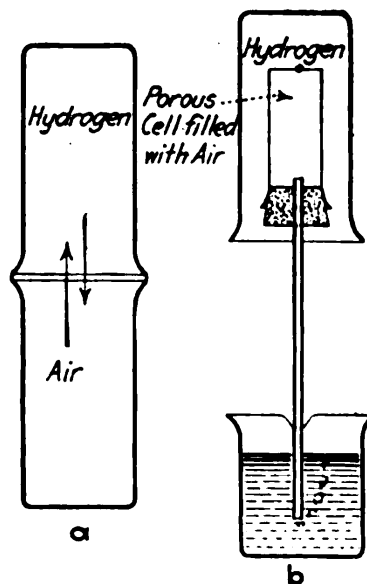


FIG. 9.

While any gas will diffuse into any other gas no matter what the difference in density may be, there is often a great difference in the velocity with which the diffusion takes place. For example, in the case of the hydrogen and air cited above, the hydrogen diffuses downward more rapidly than the air diffuses upward. In fact in all cases the less dense gas will diffuse more rapidly than the denser.

Something very nearly like this may be demonstrated qualitatively by closing a porous cell (Fig. 9b) such as is used in electric batteries, with a cork carrying a glass tube, and supporting the whole arrangement in such a way that the glass tube dips into water. If a cylinder containing hydrogen be brought over the porous cell, bubbles will quickly begin to pass out from the glass tube. This action soon ceases and if the jar of hydrogen be removed the water will begin to ascend the tube. Both effects are due to the fact that the hydrogen being less dense will pass through the porous cell more rapidly than the air, producing in the first case, some little pressure within the cell, and after the removal of the cylinder, the hydrogen passes out so much more rapidly than the air can enter that a partial vacuum results and the water rises.

The relation between the velocity of diffusion and the density is that the velocities of diffusion vary inversely as the square root of the densities of the gases.

Representing the velocities of diffusion by  $c_1$  and  $c_2$  and the density by  $d_1$  and  $d_2$  this relation may be expressed by the equation

$$c_1/c_2 = \sqrt{d_2}/\sqrt{d_1}$$

**Hydrogen and the Gas Laws.**—The gas laws which were developed under oxygen describe very accurately the behavior of hydrogen under ordinary conditions; in fact, hydrogen follows them more closely than almost any other known gas. At very high pressures, however, it is found that hydrogen does not decrease in volume as rapidly as it ought according to Boyle's law. The discrepancy becomes greater as the pressure is increased. Other gases at ordinary temperatures are usually more compressible at a moderate pressure than they should be from Boyle's law, and then at higher pressures they behave

like hydrogen and become less compressible. At higher temperatures many of them act like hydrogen and are less compressible from the start than they should be from Boyle's law. At very low temperatures hydrogen changes its behavior and is first more and then less compressible than it should be, thus behaving like the other gases.

**Liquid Hydrogen.**—Hydrogen cannot be liquefied by any pressure, however great, at ordinary temperatures, but must first be cooled to its critical temperature,  $-242^{\circ}\text{C}.$ , when it will liquefy under a pressure of 13 atmospheres. Its boiling-point under atmospheric pressure is about  $-252.5^{\circ}\text{C}.$  or only  $20.5^{\circ}\text{A}.$  By reducing the pressure to 5 cm. of mercury the temperature falls to about  $14^{\circ}\text{A}.$  or  $-259^{\circ}\text{C}.$  At this temperature hydrogen is a transparent solid. Liquid hydrogen is colorless and has a density at its boiling-point of only 0.07. It is used to get very low temperatures, since substances placed in it will be very quickly cooled to the boiling-point of hydrogen. At this temperature all other liquids and all other gases except helium become solids.

**Solid Hydrogen.**—Solid hydrogen is a transparent ice-like substance with a melting-point of  $-258^{\circ}\text{C}.$  Its density is 0.076.

**Absorption of Hydrogen by Metals.**—Hydrogen is absorbed in appreciable quantities by many metals, but especially by the rare metal palladium. Under favorable conditions, palladium will take up 900 times its own volume of hydrogen, considerable heat being evolved during the process. This hydrogen will practically all be given up in a vacuum at ordinary temperatures or it may be driven off at atmospheric pressure by warming the palladium.

The absorbed hydrogen does not enter into a chemical compound with the palladium but forms a solid solution.

**Spectrum of Hydrogen.**—When an electric discharge is passed through hydrogen under a pressure of a few tenths of a centimeter of mercury, the hydrogen glows and gives out light. This light appears rose red to the eye, but when it is examined with a spectroscope (Fig. 10), a very large number of lines are seen scattered all along from the red to the violet end of the spectrum. There are, however, four lines, red, green, blue and violet, which are much stronger than the others. Other gases under similar

conditions will give spectra but no other gas will give lines in precisely the same position in the spectrum as the hydrogen lines. These same lines will appear when hydrogen is caused to glow in any other way and their appearance is not prevented by the presence of other substances. Hence an examination of the spectrum is the surest means for the identification of hydrogen. These same lines are found in the spectra of many of the

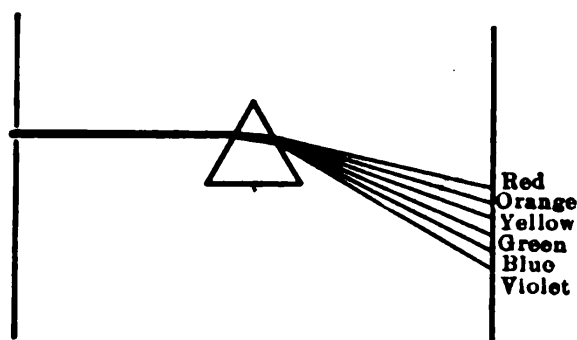


FIG. 10.

stars, and we may safely say that hydrogen is present on them as well as upon the earth (see Frontispiece).

The light from the sun and many of the stars shows dark lines at exactly the points where the hydrogen lines are bright. As will be explained, p. 293, these dark lines are due

to hydrogen, and prove the presence of this element just as certainly as the bright lines. Therefore the spectroscope shows us that hydrogen is very widely distributed throughout our universe. In much the same way it has been established that a large number of the elements known to us here are also present in the sun and stars.

**Chemical Properties of Hydrogen.**—The most marked property of oxygen is that it will support combustion vigorously. Hydrogen on the other hand will burn but not support the combustion of things which will burn in the air. This may be readily shown by bringing a lighted candle to the mouth of an inverted cylinder filled with hydrogen. The gas will take fire with a slight explosion and burn with an almost invisible flame at the mouth of the cylinder. Pass the candle up into the hydrogen and it will go out. Withdraw the candle slowly, and as the wick passes through the flame of the burning hydrogen it will be relighted.

From what we have learned of combustion in studying oxygen, we would draw the conclusion, correctly, that hydrogen will combine with oxygen. It will also enter into combination with a large number of the other elements—notably with chlorine, sulfur, nitrogen, and carbon. The conditions under which the

combination will take place, and the substances formed will be discussed in connection with the several elements.

A small stream of hydrogen issuing from a jet of platinum, or other difficultly fusible metal, burns quietly in the air with an intensely hot flame which is almost invisible. If the jet is made of glass the hydrogen flame will be colored yellow from the sodium of the glass. Water is produced by the burning of hydrogen, as may be shown by holding a glass cylinder over the flame. A dew at once appears on the glass which has all the properties of water and consequently is water. If all the water formed by the burning of a given quantity of hydrogen be collected and weighed, it will be found to weigh much more than the hydrogen itself, and therefore it follows that water is a compound of hydrogen with one or more of the constituents of the air.

If the air be replaced by pure oxygen it will be found that the hydrogen will burn even more vigorously and water will be produced as before. Hence we must conclude that water is a compound of hydrogen and oxygen and nothing else, a conclusion which is confirmed by the fact that the weight of the water formed is equal to the sum of the weights of the oxygen and hydrogen transformed.

Hydrogen and oxygen may be mixed at ordinary temperatures and no perceptible combustion will take place, but if the mixture be brought in contact with a flame or heated at any point to a temperature of about  $500^{\circ}$  to  $600^{\circ}\text{C}$ . a combination will take place very rapidly, and a flame will spread throughout the mixture almost instantaneously. The result is a rather powerful explosion due to the sudden expansion of the gases by the heat evolved during the rapid burning of the hydrogen. Because of its explosiveness, a mixture of hydrogen and oxygen in the proportion for the formation of water, *i.e.*, two volumes of hydrogen to one volume of oxygen, is called detonating gas. This detonating gas must be very carefully kept away from flames or incandescent bodies.

Because of the oxygen in the air a mixture of hydrogen and air in proper proportions is decidedly explosive. On this account hydrogen from a gas holder or from a generator should never be lighted until it has been tested and found to be pure. This may be done by collecting the escaping gas in an inverted test tube

and bringing it in contact with a flame which is kept at a distance of several feet from the hydrogen apparatus. At first the gas in the tube will behave like air, but soon it will take fire, and the flame will rush up the test tube with a whistling noise. As the trials are repeated and the gas becomes more nearly pure hydrogen, the explosions in the test tube first become stronger and then weaker until at last the hydrogen burns quietly at the mouth of the test tube for a sufficiently long time so that a flame may be carried back in this way from the burner to the hydrogen apparatus and ignite the escaping gas. This method of lighting a jet of hydrogen is perfectly safe since so long as the gas in the apparatus is explosive the explosions take place the instant the mouth of the test tube is brought to the flame, and no fire is left in the tube to ignite the jet upon the return of the tube.

**Oxy-hydrogen Blowpipe.**—Many important applications have been found for the very high temperature produced by hydrogen burning in oxygen. Because of the dangerously explosive character of a mixture of these gases it is of course out of the question to mix them in one gas holder and burn the mixture. The

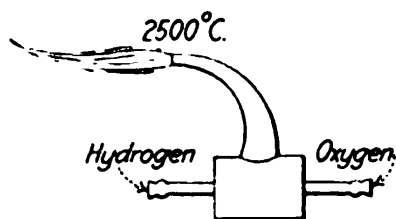


FIG. 11.

gases must then be stored separately and burned from a special burner called the oxy-hydrogen blowpipe (Fig. 11) which is so arranged that the gases are conveyed to the burner in separate tubes and mixed just before they reach the orifice of the burner. In this way

a flame may be produced whose temperature is something like  $2,500^{\circ}\text{C}$ . In this flame silver boils, iron burns, and even platinum melts. If the flame be brought in contact with a piece of lime the latter becomes intensely heated and produces an exceedingly bright light known as the calcium light, or lime light, and has often been used as a source of light for the stereopticon, but is now generally replaced by the electric arc or the nitrogen filled tungsten lamps. The oxy-hydrogen blowpipe is largely used in the autogenous welding of metals, especially of lead.

**Formation of Water from Hydrogen and Oxygen Compounds.**—If hydrogen be passed over mercuric oxide at ordinary temperatures no perceptible action takes place, but if the oxide be

gently warmed taking care that the temperature does not rise high enough to bring about its decomposition, water and metallic mercury will be rapidly formed. Hydrogen and iron oxide heated to a somewhat higher temperature will yield water and metallic iron. If tin oxide is used, metallic tin and water will be formed. Many other oxides will react in the same way with hydrogen so that we have here a rather general method for the laboratory preparation of a metal from its oxide.

A very natural inference to draw from these facts is that the hydrogen has a stronger attraction for the oxygen than the metal has, and so robs the latter of its oxygen. This conception has often been used, and the attraction is called chemical affinity. That this conception is inadequate is shown by the following case. Iron oxide and hydrogen will react at a somewhat elevated temperature for the formation of water vapor and metallic iron. And the explanation of this in terms of the above conception would be that the hydrogen had a greater affinity for the oxygen than the iron had. But as was mentioned on p. 33, if water vapor be passed over metallic iron heated to the same temperature used in the above case, hydrogen and iron oxide will be formed. The explanation of this would be that the iron had a greater affinity for the oxygen than the hydrogen had and so robbed the water of its oxygen. The action in the one case is just the reverse of that in the other and of course it cannot be that the iron has both a greater and a less affinity for oxygen than hydrogen has. Nor can the reversal be due to change in affinity due to the difference in temperature because the reactions both take place at the same temperature. From this it can be seen at once that the explanation must be either abandoned or modified.

Such actions as these we have just been discussing are called reversed or reversible reactions and are very common in chemistry. In fact they are more commonly met with than the irreversible reactions or those which go only in one direction. A careful study of these reactions is desirable because of their frequent occurrence, and also the ease with which they may be controlled when once understood.

Probably the best way to obtain an understanding of reversible reactions is to consider them as being composed of

substance merely by its presence increasing the rate at which a reaction takes place. (See case of manganese dioxide and potassium chlorate, p. 17.) Some other metals have the same property although to a smaller degree than platinum and it is very common to find that the rate of a reaction is greatly altered by the presence of a substance which is not changed by the reaction. We call actions of this kind catalytic actions. The substance through whose presence the rate of action is altered is called a catalyzer, and the whole process is spoken of as catalysis.

Some catalyzers act as platinum does in this case and increase the rate of reaction; these are called positive catalyzers. Others decrease the rate of reaction and are known as negative catalyzers. Catalyzers simply alter the rate at which a reaction is taking place and cannot bring about one which is not already going on. Cases of catalysis are of very frequent occurrence and will be often mentioned in the course of this work.

## CHAPTER V

### WATER

Water is one of the most important as well as one of the most widely distributed substances in nature. Some idea of its abundance may be gathered from the fact that the ocean contains about 300,000,000 cubic miles of water and each cubic mile weighs over 4,000,000,000 tons. Liquid water covers 72 per cent. of the earth's surface; the atmosphere contains enormous quantities of water in the gaseous state, and the polar regions and the tops of lofty mountains are covered with solid water or ice. The crust of the earth is everywhere permeated by water, and all living organisms, both plants and animals,

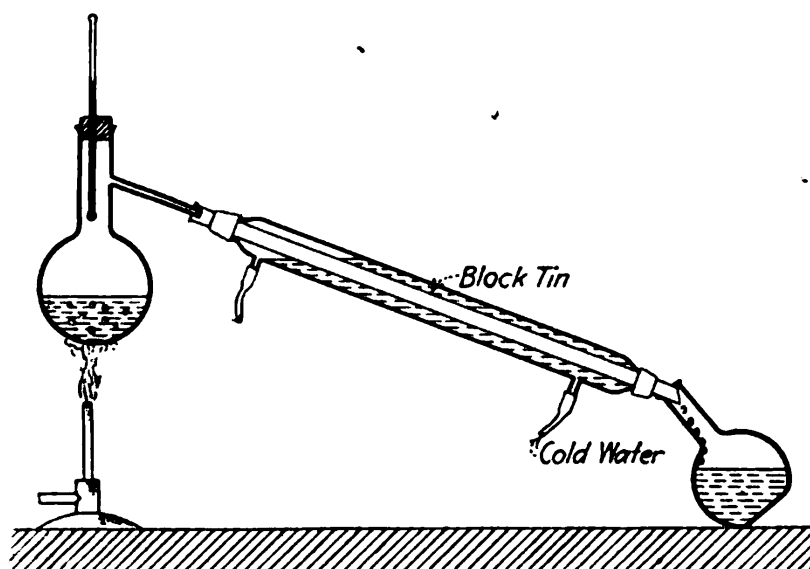


FIG. 13.

contain water as an absolutely essential portion of their structure. The human body contains about 70 per cent. and the ordinary foods from 35 to 95 per cent. water.

Water is a very good and general solvent and takes up more or less of nearly everything with which it comes in contact. Water is usually purified by the process of distillation which consists in heating the water until it boils and is converted into

vapor and then, in a separate vessel (Fig. 13), cooling the vapor and reconvertng it into water. Most of the substances present in the impure water are much less easily vaporized than water and are left behind when the latter is boiled. Some impurities, such as ammonia and carbon dioxide, are more volatile than water and pass over with the first portions of the vapor. By rejecting the first part of the distillate, practically pure water may be obtained. Absolutely pure water cannot be prepared because it must come in contact with a vessel of some kind, and it will inevitably dissolve some of the latter, thus rendering the water impure. Stills and condensers of platinum or pure block tin are least attacked and give the purest water.

For drinking purposes the dissolved impurities in natural fresh waters are not so important as the bacteria which they carry. Since the latter are in suspension and not in solution, they may be removed by very fine-pored filters, and in a sense the water is thereby purified. The same result may be obtained by killing the bacteria by ozone (see p. 30), or by bleaching powder (see p. 129), or by boiling.

**Physical Properties of Water.**—It is at ordinary temperatures a transparent, almost colorless liquid with a faint bluish tint which becomes apparent upon looking through a thick layer of water. This color can be seen in clear lakes and in the ocean.

Most substances increase in volume more or less regularly with rising temperature, but water is a decided exception. If one starts from 0°C. and warms the water its volume will decrease until a temperature of 4°C. is reached, and then with rising temperature the volume increases. Since the density of a substance varies inversely as its volume, the temperature of maximum density of water is 4°C.

The following table gives some of the values for the density of water at different temperatures:

Temperature	Density	Temperature	Density
0° C.	0.99987	40° C.	0.99224
4° C.	1.0000	60° C.	0.98324
10° C.	0.99973	80° C.	0.97183
20° C.	0.99823	100° C.	0.95838

**Ice.**—At a temperature of  $0^{\circ}\text{C}$ . water changes from the liquid to the solid state and is then known as ice. This change is on the border line between physical and chemical changes; so many of the properties of ice are different from those of water, as will be seen from what follows, that it may properly be considered a chemical change, and yet the transformation back and forth takes place so easily that many regard this as a physical change.

**Properties of Ice.**—Ice is a transparent solid of a faint bluish color which is seen only in large masses such as icebergs or glaciers. It is such a poor conductor of electricity that it becomes electrified when rubbed. Ice is almost twice as good a conductor of heat as water, but even then it is a very poor conductor.

The density of ice at  $0^{\circ}\text{C}$ . is 0.91674, which is much smaller than that of water at the same temperature which is 0.99987. This means that on freezing water increases nearly one-eleventh in volume, and also that ice will float on water. In these respects water is somewhat unusual, since most substances decrease in volume upon solidification, and the solid sinks in the liquid.

In all climates where freezing and thawing take place, the great increase in volume when the water passes into ice has played a very important part in the disintegration of rocks. When the rain falls upon the rocks it fills even the small cracks. Upon freezing the increase in volume forces the crack to widen. When the ice melts the water runs down in the crack, and upon freezing spreads the pieces of rock still farther apart until presently the rock is split up under the repeated action of the freezing and thawing of the water. The bursting of water pipes when the water in them freezes, and the loosening of the soil in the winter time are due to this same cause.

Ice is a crystalline substance, and crystals may be defined as bodies many of whose properties vary with the direction in which they are measured. As a result of this variation a crystalline substance tends, when it takes on the solid state, to form bodies whose limiting surfaces meet at perfectly definite angles, and so build up regular polyhedral forms. All other physical properties which can possibly do so vary with the

direction in which they are measured. Some of these properties are conductivity for heat and electricity, velocity of light, elasticity, etc.

Those solids which are not crystalline are called amorphous substances, and glass is a good example of such a substance. All the properties of glass are the same in every direction. The property of forming crystals is very common among pure solid substances, while most amorphous substances are mixtures.

Well-formed crystals often grow on the surface of water, but the best are found in the snow because they have been formed in the air with nothing to interfere. The snow crystals usually appear as six-pointed stars.

Water in contact with ice cannot be cooled below  $0^{\circ}\text{C}$ . nor warmed above this temperature, but so long as there is present an intimate mixture of ice and water the temperature is  $0^{\circ}\text{C}$ . For this reason the ice point is generally used for a standard temperature.

In the absence of ice, water may be cooled a number of degrees below zero without freezing. In this condition it is said to be **supercooled**. It is interesting to note that while water is cooling down from  $0^{\circ}$  it continues to expand just as it does from  $4^{\circ}$  to  $0^{\circ}$ . In fact there is no sudden change in the properties of water at  $0^{\circ}$  except that at that temperature it becomes possible for ice to exist which it cannot do at higher temperatures. Water which has been cooled to a few degrees below zero is stable toward all kinds of changes except the introduction of ice. Let the very smallest piece of ice come in contact with the water and freezing at once starts and the temperature rises to  $0^{\circ}\text{C}$ .

If a test tube partially filled with ordinary distilled water be supported in a freezing mixture of ice and salt in such a manner that the surface of the water in the tube is a centimeter or so above the surface of the freezing mixture, the water will supercool several degrees. By taking elaborate precautions water has been supercooled to  $-15^{\circ}\text{C}$ .

**Heat of Fusion.**—Whenever any liquid substance solidifies, heat is evolved; and conversely when a solid melts heat is absorbed. The heat absorbed during the melting of 1 grm. of a solid without raising its temperature is called the heat of fusion of that solid. That evolved during the freezing of unit mass of

he substance is called the heat of solidification. These heats are of equal numerical value and are both often called the heat of fusion. Ice behaves like all other solids in these respects and is only noteworthy because its heat of fusion is greater than that of any other substance except ammonia.

**Measurement of Heat.**—A quantity of heat is measured by determining the change in temperature which it will produce in a known weight of water; the heat capacity of the water, *i.e.*, the number of joules required to raise the temperature of 1 gm. of water  $1^{\circ}$ , having been carefully determined. The heat capacity is also known as the specific heat and varies somewhat with the temperature. Another unit is that quantity of heat which raises the temperature of 1 gm. of water  $1^{\circ}\text{C}$ . This is called the small calorie (abbreviated "cal."). Since the specific heat of water varies with the temperature, it is necessary to specify the temperature of the water. A larger and very generally used unit is the large or kilogram calorie. It is the heat necessary to rise the temperature of 1 kgm. of water  $1^{\circ}\text{C}$ . It is abbreviated Cal. and equals 1,000 small calories.

The heat of fusion of ice, that is, the heat required to melt 1 gm. of ice, is 334 joules or 80 cal. If, therefore, 80 gm. of water at  $1^{\circ}$  be mixed with 1 gm. of ice, 81 gm. of water at  $0^{\circ}$  will be produced.

In technical work in England and the United States, another unit for the measurement of heat is in use. It is known as the British thermal unit and is abbreviated B.t.u. It is the quantity of heat required to raise the temperature of 1 lb. of water  $1^{\circ}\text{F}$ .

The relation between the small calorie and the erg has been carefully worked out by Joule and others, and a small calorie at  $15^{\circ}$  is equal to 41,880,000 ergs or 4.188 joules.

The fact that the temperature of a mixture of ice and pure water is always  $0^{\circ}$  finds its explanation in this heat of fusion. If heat is applied to the mixture, instead of raising the temperature some of the ice melts and absorbs the heat. If heat is taken away from the mixture, instead of the temperature's falling some of the water freezes and supplies the heat. Because of the constancy of this temperature ice finds many applications in science. Because of its cheapness, its great heat of fusion, and

its rather low melting-point, enormous quantities of ice are used in every day life for the preservation of food since the destructive changes take place much more slowly in the food cooled by ice than at ordinary temperatures. They are like all other chemical changes in that they are slowed down by lowering the temperature.

When ice and common salt are brought together a solution results, the freezing-point of which is much lower than  $0^{\circ}\text{C}$ . This is the basis of the use of ice and salt for freezing ice cream, etc. By using three parts of ice to one of salt a temperature of  $-18^{\circ}\text{C}$ . can be obtained; this was taken by Fahrenheit as the

zero point for his thermometer. The common salt may be replaced by other soluble substances because the freezing-point of any solution is lower than that of the pure liquid. Most substances will not give as low a temperature as salt, but a few will give even lower. However, because of its cheapness and convenience salt is the best to use. The use of salt for the removal of ice and snow from sidewalks, etc., depends upon this same phenomenon.

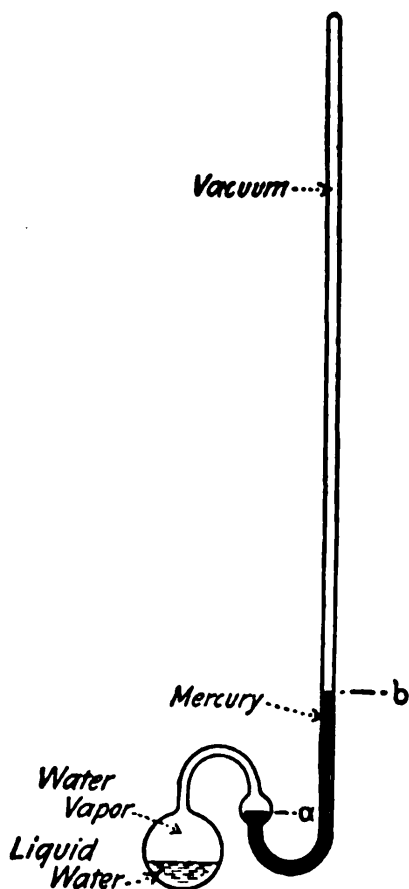


FIG. 14.

**Gaseous Water.**—Both water and ice are very easily transformed into gaseous water which is commonly known as water vapor at ordinary and as steam at higher temperatures, although there is no real difference between them. To bring about this transformation, all that is necessary is to introduce the water or ice into a vessel which it does not entirely fill. Under these circumstances

the formation of the gaseous water will begin at once and the vapor will soon fill all the space unoccupied by the other modification. The transformation of water or ice into water vapor is called evaporation. Water vapor is a gaseous substance and its behavior is fairly well described by the gas laws. This is particularly the case if the pressure is low.

Like all other gaseous substances, it exerts a pressure upon the walls of the containing vessel, and experiment shows that when water is brought into a space which it does not fill, evaporation takes place until either all the water has been converted into vapor or the pressure of the water vapor has reached a certain definite limit. This limit varies with the temperature but is always the same at any given temperature, and is entirely independent of the shape or size of the vessel or the relative volume of the liquid or the solid and the water vapor. We are dealing here then with a state of equilibrium between the water vapor and the liquid water or the ice. The limiting pressure at which the water vapor is in equilibrium with the other modification is called the **vapor pressure** of the water, or of ice as the case may be. It may be measured in the apparatus shown in Fig. 14. The vertical distance from *a* to *b* measures the vapor pressure.

The following table gives the vapor pressure of water at different temperatures:

VAPOR PRESSURE OF WATER

Temperature C°	Pressure in cm.	Temperature C°	Pressure in cm.	Temperature C°	Pressure in cm.
0	0.46	25	2.35	70	23.38
5	0.65	26	2.50	80	35.55
10	0.92	27	2.65	90	52.60
15	1.27	28	2.81	95	63.40
20	1.74	29	2.98	96	65.77
21	1.85	30	3.16	97	68.21
22	1.97	40	5.50	98	70.73
23	2.09	50	9.22	99	73.32
24	2.22	60	14.92	100	76.00

From Dalton's law of partial pressures and the fact that water vapor is gaseous, it can be readily seen that the vapor pressure of water will be the same whether the evaporation takes place in a vacuum or into a space filled with gases which do not dissolve to any marked degree in water. If the gases are very soluble they will alter the water, and hence the vapor pressure of the water.

When heat is applied to water in an open vessel, the temperature of the water gradually rises and finally small bubbles of gas appear in the liquid, rise to the surface and burst. These small bubbles consist of the gases dissolved in the water and of water vapor. The temperature continues to rise and these small bubbles are replaced by larger ones which consist of water vapor alone. This phenomenon is then called boiling. After the water has begun to boil, the temperature does not rise.

A little reflection will convince one that a bubble of vapor down in the body of the liquid must be under a pressure equal to that of the atmosphere plus that due to the column of liquid above it, and that due to the action of surface tension.

The vapor pressure of the boiling liquid must be equal to these. Neglecting the last two factors which are usually small, we may say that *the boiling-point of a liquid is the temperature at which the vapor pressure of the liquid is equal to the atmospheric pressure*. Since the boiling-point is the temperature at which the vapor pressure of the liquid is equal to the external pressure, the boiling-point will vary as the pressure changes, and will rise as the pressure is increased. The boiling-point of water under a pressure of one atmosphere is  $100^{\circ}\text{C}.$ ; at two atmospheres the boiling-point is  $121^{\circ}\text{C}.$ ; under ten atmospheres it is  $180^{\circ}\text{C}.$ , and continues to rise up to the critical point when the boiling-point of water is  $374^{\circ}\text{C}.$  under a pressure of 200 atmospheres. By lowering the pressure, water may be made to boil at temperatures below  $100^{\circ}\text{C}.$  With the aid of a good water vacuum pump, water may be made to boil at temperatures below  $30^{\circ}\text{C}.$  If the pressure be reduced to less than 0.4 cm. of mercury, the boiling-point will fall below the freezing-point, and the water will freeze and boil at the same time.

Use is often made in the laboratory of the fact that the temperature of water boiling in an open vessel, and also the steam from it is never far from  $100^{\circ}\text{C}.$  For example it is often necessary to heat a substance to about  $100^{\circ}\text{C}.$  and at the same time absolutely essential that the temperature shall not go higher. This can be easily done by heating it on what is known as a water bath. The simplest form of a water bath consists of a beaker half full of water and loosely covered with an evaporating dish

or other suitable vessel containing the substance to be heated. If now the water be boiled, the steam will come in contact with the dish and quickly raise the temperature to about  $100^{\circ}\text{C}$ . but never above the boiling-point of water at the pressure of the atmosphere.

**Humidity of the Air.**—From the very wide distribution of liquid water upon the earth's surface, it of course follows that water vapor is always present in the air. One might expect that the partial pressure of water vapor in the air would be equal to the vapor pressure of the water. However, this is rarely the case because the temperature of a body of water is usually lower than that of the surrounding land area, and even if the partial pressure of the water vapor in the air over the water becomes as great as the vapor pressure of the water at the temperature of the water, as soon as the air moves over the land, its temperature will rise and the partial pressure of the water vapor will then be less than the vapor pressure of the water at the temperature of the air. This is sometimes expressed by saying that the air is only partially saturated, carrying the idea that the air dissolves the water much as water dissolves salt. The notion is only partly correct. The term "relative humidity" is often used in this connection and is the ratio of the partial pressure of the water vapor in the air to the vapor pressure of water at the temperature of the air.

The water vapor in the air is of great consequence in chemistry because of the fact that everything which is exposed to the air takes on more or less water. Some things take on so much water that they pass into a liquid solution or deliquesce, while others simply condense a thin film of water upon their surface. This last is the behavior of glass and other substances that do not dissolve. This water condensed upon the surface often gives a great deal of trouble in making accurate weighings, because of the fact that it will vary markedly with the relative humidity and temperature of the air. The most efficient way to remove this film of liquid water is to heat the object and drive the water off as vapor. However, it must be noticed that a film of water does not behave exactly like liquid water in that its vapor pressure is very much smaller than that of liquid water at the same temperature, and consequently the temperature has to be very

high to remove the water thoroughly. In some cases it is not possible to heat the object to drive off the water, and in this case it must be placed in a closed vessel called a desiccator which contains one of the drying agents already mentioned. Under these conditions, the water will vaporize from the object and slowly diffuse to the desiccating substance. The process is a very slow one and will be greatly hastened by removing the air, since the latter interferes with the diffusion of the vapor.

**Heat of Vaporization of Water.**—Whenever any liquid, water included, passes into the gaseous state heat is absorbed unless the transformation takes place at the critical point. This absorption of heat is not accompanied by a rise in temperature and simply represents the difference in energy between the liquid and the gaseous substance and the work done in the transformation. This absorption of heat is often ascribed to the work done in separating the particles of water from each other, since gaseous water occupies a very much larger volume than the liquid water from which it was formed. However, this cannot be the explanation because there is an increase in volume when water freezes, and yet heat is given out in this case. The heat absorbed in the transformation of 1 gm. of a liquid into its vapor, without rise in temperature, is called its heat of vaporization. In the case of water it is 537 cal. or 2,245 joules at 100°C. or 606.5 cal. or 2,535 joules at 0°C. So as the temperature rises, the heat of vaporization decreases and becomes zero at the critical temperature.

Steam is extensively used for the heating of buildings, because such large quantities of heat may be transmitted with the movement of only a small amount of substance.

**Effect of Pressure on the Melting-point of Ice.**—Ice and water exist in equilibrium over a certain range of temperature and pressure, for each temperature there is a perfectly definite pressure of equilibrium. Experiment has shown that the melting-point of ice is lowered by 0.0072° for each atmosphere by which the pressure is increased. An increase in the pressure of 139 atmospheres is required to lower the temperature 1°C. A mixture of ice and water then, can have a temperature of 0°C. only when under a certain pressure. By definition of 0°C. this is the standard pressure. A change in the barometric pressure should then affect the melting-point of ice and the alteration

should amount to about  $0.0001^{\circ}\text{C}.$  for a change in the barometric pressure of 1 cm.

Although the lowering of the temperature for each atmosphere increase of pressure is very small, it is possible by pressure alone to keep water in the liquid state at  $-24^{\circ}\text{C}.$  The pressure necessary for this may be most readily obtained by freezing a part of the water contained in a very strong steel vessel. The freezing of only a small part of the water will produce an enormous pressure because of the marked increase in the volume of water when it is changed into ice.

**The Law of Mobile Equilibrium.**—The melting-point of practically every solid is altered to some extent by a change in pressure. An increase in pressure lowers the melting-point of some few but raises that of most substances. In every case an increase in pressure causes some of the less dense form of the substance to change into some of the denser form, and so produces a contraction which tends to relieve the pressure. To maintain a balance under such conditions between the relative quantities of the two forms, the temperature must be altered in such a direction as will of itself tend to produce more of the less dense form. Usually the solid is denser than the liquid, and the tendency is for it to form when the pressure is increased. So the melting-point of most substances is raised. The case is just the other way around with water for the ice is less dense than the water and the melting-point is lowered. In every instance we are dealing with an equilibrium between a solid and a liquid, and the shifting of this equilibrium under the action of a constraint in the form of pressure. The equilibrium is always shifted in such a way that the pressure tends to be relieved. These are special cases of a very general law which applies to all kinds of equilibria both physical and chemical. This law may be stated as follows: *If a constraint is put upon a system in equilibrium whereby the equilibrium is altered, that reaction will follow which tends to decrease the constraint.*

**Solutions.**—It is a matter of every-day experience that many substances will dissolve in water. We call these water or aqueous solutions of the substances. A solution, it will be recalled, is a homogeneous mixture of two or more substances, the relative proportions of which may vary continuously within

certain limits and whose properties vary with the proportions of the components. Solutions may exist in all three of the physical states, and it is simply the circumstance that we are so familiar with water solutions that makes us tend to think of a solution as a liquid.

In connection with solutions two terms, solute and solvent, are in constant use, and their meaning should be understood. The substance which is dissolved is called the solute, while that in which the solute is dissolved is called the solvent. A solution of salt in water is obtained by dissolving the solute salt in the solvent water. The solute may be solid, liquid, or gaseous, and so may the solvent. As an example of a liquid dissolving in a gas, we may take the vaporization of water into air.

Aqueous solutions are of great importance in chemistry because of the fact that many chemical processes take place very readily in them; one reason for this being, apparently, that the water will bring together into one liquid, solid, liquid or gaseous solutes in the very most intimate mixture.

In general, solutions have properties which are a sort of mean between the properties of the two components, so these aqueous solutions will have in the main the properties of water. One very important circumstance to note about solutions is that a solute always lowers the vapor pressure of its solvent upon passing into solution. From this it follows that if the solute is non-volatile, the vapor pressure of the solution will always be less at any given temperature than the vapor pressure of the pure solvent. In case the solute is volatile, the partial pressure of the solvent is lowered as before, but the vapor pressure, which is the sum of the partial pressures of the solvent and of the solute, may or may not be lower than that of the solvent in the pure state. For solutions which are dilute, the lowering of the vapor pressure is proportional to the mass of the solute dissolved in a given fixed mass of the solvent, at constant temperature.

In Fig. 15, the curve AOB is the vapor pressure curve for the pure solvent, and the curve CO'D that for the solution. It will be noticed that the curve for the solution lies below that for the solvent, and that they are not parallel. The curve EO'O is the vapor pressure curve for the ice. The line MN represents the atmospheric pressure. From the definition of boiling-point it

will be seen that the temperature corresponding to the points B and D represent the boiling-points of the pure solvent and of the solution respectively. This also shows that owing to the decrease in the vapor pressure caused by the solute, the boiling-point of the solution is higher than that of the solvent. This is true in every case where the solute is non-volatile. If the solute is volatile, the boiling-point of the solution may be higher or lower than that of the pure solvent depending upon whether the partial pressure of the solute is less than or greater than the lowering of the vapor pressure of the solvent.

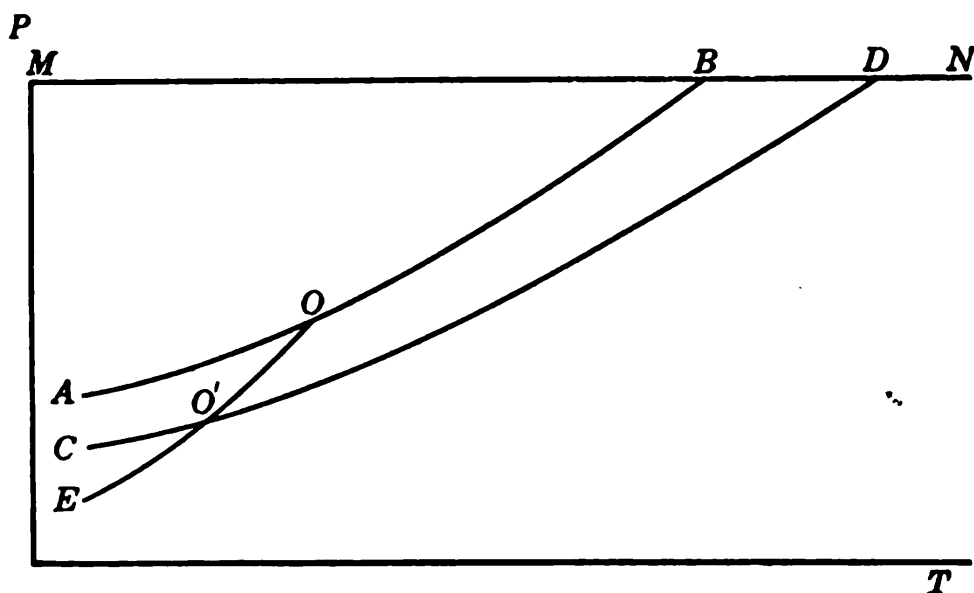


FIG. 15.

The freezing-point of all solutions from which the solvent separates as a pure solid is lower than that of the pure solvent. In order to understand this, it will be necessary to consider the relations between the vapor pressure of the solid and of the liquid. It seems very natural to assume that ice has no vapor pressure, but this is a mistake for ice has a measurable vapor pressure even when cooled to many degrees below zero. This pressure is 0.46 cm. at zero degrees, and becomes smaller as the temperature falls. As may be seen by reference to Fig. 15, the vapor pressure curve for ice is not a continuation of that for water, but lies below the water curve except at point O, where the curves meet. It is only at this point, O, then that the solid and liquid have the same vapor pressure and can be in equilibrium with each other. At temperatures below

this point the vapor pressure of the water is higher than that of the ice and a little thought will convince anyone that the two could not continue to exist side by side because the water would evaporate and condense on the ice as the solid, and this would go on until all the water had disappeared. A little reflection will show that a system must be in equilibrium in every way to be in equilibrium in any way. Therefore it follows that since at the freezing-point the solid and the liquid are in equilibrium, the vapor pressure of the two must be the same. We may then frame a definition of the freezing-point so that it shall be similar to that for the boiling-point. The freezing-point of a substance is the temperature at which the vapor pressure of the solid is the same as that of the liquid modification. In Fig. 15 this is at the point O, where the two curves AOB and EO'O cut. Correspondingly the freezing-point of the solution will be the temperature at which the vapor pressure of the solution equals that of the ice,<sup>1</sup> and this will be at the point, O', on the curves and will always be at a lower temperature than that of the pure solvent. From these considerations it will be seen that the solute lowers the vapor pressure of the solvent and that this results in the solutions boiling at a higher, and freezing at a lower temperature than the pure solvent. No real explanation for the lowering of the vapor pressure can be given, but we can picture it to ourselves by assuming that things dissolve because they have an attraction for each other, and that, because of this attraction the solvent finds it more difficult to pass over into the gaseous state from a solution than when it is pure.

When a solid salt is brought into contact with water, some of it dissolves. If the salt is difficultly soluble, like silver chloride, the weight of the salt which a given weight of water, say 100 grm., can take up is very small indeed; but in the case of an easily soluble compound like calcium chloride, the mass which can be dissolved by the same weight of water is very large. However, there is at each temperature and pressure a definite limit to the weight of a salt which a given weight of water will dissolve. A solution in which this limit has been reached, and

<sup>1</sup> The student should remember that when a solution freezes the solid which separates almost always consists of crystals of the pure solvent and not of the solution.

which is in equilibrium with some of the solid solute, is called a saturated solution. The ratio between the weights of the solute and the solvent in a saturated solution is called the solubility of the solute. It is usually expressed in terms of parts by weight of solute in 100 parts by weight of solvent.

As a rule the solubility of a salt is markedly altered by changes of temperature. Generally, but by no means always, the solubility increases with rising temperature. The solubility is very much less sensitive to changes in pressure than to changes in temperature, in fact it requires a change in the pressure of hundreds of atmospheres to make a measurable change in the solubility. So small is the influence of pressure that for all practical purposes it may be neglected.

If less of the salt be added to the solvent than it is capable of dissolving, all will be taken up. The solution is said to be unsaturated because it can still take up more of the salt. If more of the salt be added than the solvent can dissolve, that quantity which corresponds to the solubility will pass into solution and the excess will be left undissolved. The concentration of the salt in solution is absolutely independent of whether this excess be large or small.

Just as a liquid may be supercooled if the solid modification be excluded, so a solution may be prepared which contains more of the solute than corresponds to its solubility if the solid solute is not present. Such solutions are called supersaturated. In the absence of the solid solute, they are stable toward most changes; but when brought in contact with even a very small piece of the solid, all the excess of solute over that corresponding to its solubility quickly separates out in the solid form.

**Application of the Law of Mobile Equilibrium.**—We must go to the law of mobile equilibrium for information as to the direction of the change of solubility for a given change in temperature or pressure.

This law says that if a system in equilibrium is subjected to a constraint whereby the equilibrium is altered, that reaction will follow which tends to relieve the constraint. If the constraint consists in the addition of heat whereby the temperature of the system is raised, the change which will follow will be accompanied by the absorption of heat. If a salt dissolves in its almost

saturated solution with the absorption of heat, more salt will pass into solution when the system is heated. In other words, the solubility of the salt increases with rising temperature. On the other hand, if a salt dissolves in its almost saturated solution with the evolution of heat, it will pass out of solution into the solid state with the absorption of heat. So if such a solution be heated, solid salt will separate as the temperature rises, or the solubility will decrease with rising temperature. A salt which dissolves without any heat effect will not change its solubility with the temperature. This is very nearly true of sodium chloride. The heat of solution of a salt in its saturated solution is often very different, not only in magnitude but also in sign, from its heat of solution in the pure solvent. It is only the former heat effect which is of significance in this connection.

If the pressure be increased, that change will take place which is accompanied by a decrease in volume, since this will tend to relieve the pressure. The solubility of the salt will increase with the pressure in case the more concentrated solution has a smaller volume than the saturated solution together with the solid salt. But if the volume of the system would be decreased by the separation of the solid salt, the solubility of the salt will decrease with increasing pressure.

**The Chemical Properties of Water.**—Water can react chemically in essentially two different ways, that is, it may combine directly, in which case only one new substance is formed, or it may react because of its being a compound of hydrogen and oxygen. In this case two or more new substances are formed. As examples of direct combination, we might cite the union of water with lime (calcium oxide) to form calcium hydroxide; with anhydrous copper sulfate to form crystallized copper sulfate or blue vitriol; with anhydrous calcium chloride to form crystallized calcium chloride. These compounds of water and the salts such as the copper sulfate and the calcium chloride are called hydrates or salts with water of crystallization. The hydrates differ greatly in their stability, and some are so easily decomposed into water and the rest of the compound that many have been led to believe that they are essentially different from other chemical compounds, and that the water exists in them in some peculiar way as water. They have, however, all the

characteristics of chemical compounds, that is, follow the law of definite proportions, differ radically in their properties from their components, etc., so there is no reason for setting up a special class for these substances.

As cases of the behavior of water as a compound of hydrogen and oxygen, we may call to mind the reactions between water and iron, or magnesium, calcium or sodium whereby hydrogen and a compound of the metal with oxygen or with oxygen and hydrogen are formed. It is important to notice in this connection that it is much more difficult to decompose water into its elements than it is such a compound as mercuric oxide; on this account water is called a stable substance.

**The Reaction of Sodium and Water.**—The action of sodium upon water is so very vigorous that only very small quantities of sodium, a piece not larger than a pea, should be used at a time. Larger quantities are very likely to produce explosions, from the very great volumes of gas and steam liberated, which are as violent as those due to an equal weight of dynamite. When sodium acts upon water, hydrogen and a solution of sodium hydroxide are formed. Sodium hydroxide is a white easily soluble solid which is a highly caustic alkali and hence is often called caustic soda. When sodium hydroxide is exposed to the air, it becomes moist and finally passes into a liquid which is identical in its properties with a strong water solution of the substance and hence is such a solution. The water necessary for the formation of this solution comes from the air. Sodium hydroxide and things like it which take up water vapor from the air and form solutions are called **deliquescent substances**. All such substances are very freely soluble and have the common characteristic that their saturated solutions give a smaller vapor pressure of water than the partial pressure of the water vapor in the air. If this were not so the substance could not deliquesce. Many of the salts containing water of crystallization decompose readily into their components and give an easily measurable vapor pressure of water. If the partial pressure of the water vapor in the air is less than the vapor pressure of the water from the salt, the latter will decompose and the crystals will fall to powder. The substance is then said

to effloresce. At any given temperature the vapor pressure of a saturated solution of a substance or that of water from a hydrate is constant, but the partial pressure of the water vapor in the air varies from time to time, so a substance may deliquesce one day, be stable the next, and even effloresce on the day after; its behavior being determined by the partial pressure of the water vapor in the air and the vapor pressure of the water from the substance.

In ordinary weather calcium chloride will deliquesce, and even after the salt has all dissolved, the solution will continue to take up water from the air until the partial pressure of the water vapor in the air is equal to the vapor pressure of the solution. If such a solution be allowed to stand in the laboratory until winter comes on, it will be found that the water will gradually evaporate and finally crystals of calcium chloride with water of crystallization will form. In the depth of winter these crystals sometimes fall to a powder or effloresce. So calcium chloride is both a deliquescent and an efflorescent substance. The explanation being of course that in the summer the partial pressure of the water vapor in the air is high, while in the winter it is low indoors on account of the low temperatures prevailing outside.

**The Composition of Water.**—Water is, of course, a chemical compound of hydrogen and oxygen and hence from the law of definite proportions the relative proportion by weight in which these elements combine to form water will be fixed and invariable. This proportion is a very important property, not only of hydrogen and oxygen, but also of water.

There are two general methods of procedure for determining the composition of a substance. We may decompose the substance into its elements and determine the proportion by weight in which each is present. ~~This is called analysis.~~ Or we may bring together the elements which go to make up the substance and make the conditions such that they will combine to form the desired compound. By carefully noting just what weight of each element disappears in the formation of a given weight of the compound, the quantitative composition of the substance may be determined. ~~This is called synthesis.~~

For the analysis of water, advantage may be taken of the fact

mentioned under the discussion of the methods for the preparation of hydrogen, that when a current of electricity is passed through water between two plates of platinum, hydrogen appears at one of the platinum plates and oxygen at the other. In this process the platinum plates are unaffected, and the weight of the hydrogen plus the weight of the oxygen equals the weight of the water which disappears, thus showing that these substances are the only ones formed in the process. By collecting the gases separately and determining their weights, a quantitative analysis of the water may be made. Since the densities of the gases are known, it is not necessary to weigh them; all that is required is that their volumes be measured under known conditions of temperature and pressure (Fig. 16), and from these data the volumes under standard conditions may be readily calculated. The volumes under standard conditions times the densities of the gases will, of course, give the weights of the gases, and therefore the proportion by weight in which they combine to form water which is the result desired.

When this operation is performed it turns out that if the gases be measured under the same conditions of temperature and pressure, that the volume of hydrogen is almost exactly twice that of the oxygen. The ratio according to the best determinations being 2.0025 volumes of hydrogen to 1.0000 volume of oxygen. The density of hydrogen is 0.00008986 and of oxygen 0.0014293 and therefore the ratio by weight is  $2.0025 \times 0.00008986$  divided by  $1.0000 \times 0.0014293$ , or 1.000 of hydrogen to 7.943 of oxygen or roughly 1 to 8. The percentage composition of water is then 11.19 per cent. hydrogen and 88.81 per cent. oxygen.

One of the standard methods which has been much used for the quantitative synthesis of water is based upon the reaction taking place between copper oxide and hydrogen at a somewhat elevated

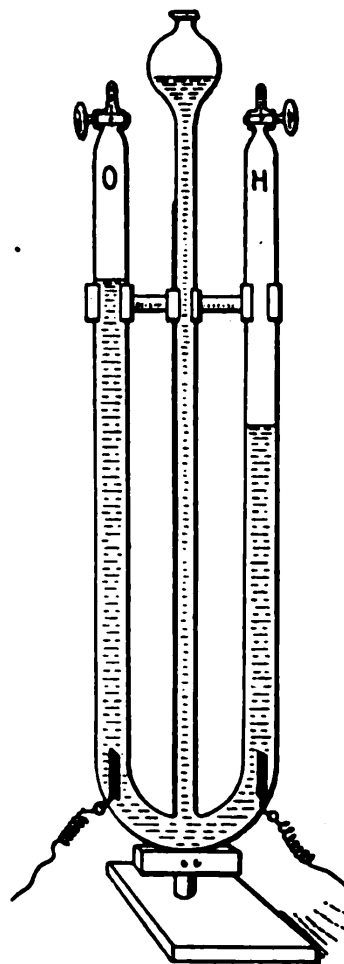


FIG. 16.

temperature whereby water and copper are produced. The process may be briefly outlined as follows: Pure dry hydrogen (Fig. 17), is passed over a weighed quantity of copper oxide at a little below the temperature of redness. The water formed is collected by absorption in a weighed quantity of calcium chloride. The increase in weight of the calcium chloride at the end of the experiment over that at the beginning gives the weight of the water formed. The difference between the weight of the copper oxide and of the copper formed from it gives the weight of the oxygen which was transformed into the water. The difference between the weight of the water and that of the oxygen is, of course, the weight of the hydrogen. The composition of water from data obtained in this way checks very closely with that given above.

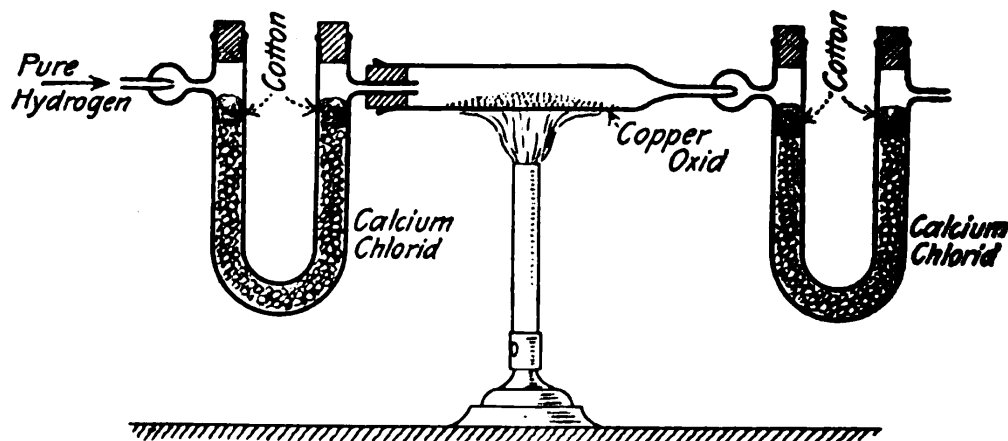


FIG. 17.

Another method for the quantitative synthesis of water consists in determining the proportion by volume in which hydrogen and oxygen unite to form water. From this ratio and the densities of the gases, the proportion by weight may be easily obtained as was shown above. Since a mixture of hydrogen and oxygen may be caused to explode by passing an electric spark through the mixture at any point this synthesis is very easily carried out. The apparatus necessary consists of a thick-walled glass vessel (Fig. 18), strong enough to stand the explosion of the gases and having two platinum wires sealed through its walls. Carefully measured volumes of hydrogen and of oxygen are introduced into the vessel, mixed and exploded. The residual gas is then measured and examined

to see whether it is hydrogen or oxygen. The results show as before that the gases combine in the proportion of very nearly two volumes of hydrogen to one of oxygen. If the gases are mixed in just this proportion no residue is left; but if an excess of either one is used, the excess of that gas is left unchanged. If this synthesis is carried out at temperatures above the boiling-point of water and at pressures somewhat below that of the atmosphere so that the water formed shall stay in the gaseous state, as water vapor, the volume of this water vapor is very nearly the same as that of the hydrogen from which it was formed, both measured at the same temperature and pressure. So the following very simple relation exists between the volumes of the gaseous substances involved in this reaction: two parts by volume of hydrogen will combine with one part by volume of oxygen to form two parts by volume of water vapor, all being measured under the same conditions of temperature and pressure.

When other gases enter into reaction with one another, relations between the combining volumes are always very simple, often even simpler than in the case given above. This behavior of gases is described by the law known as **Gay Lussac's law of the combining volumes of gases**. *Whenever in any chemical reaction two or more gases appear or disappear, they do so in the ratio of small whole numbers by volume.* In the case given above, the ratios are 2:1:2.

When we come to compare the proportions by volume in which solids or liquids react, we find no suggestion of the existence of a simple relation, nor is there any simple proportion by weight in which substances react. We find here another instance of the great simplicity of the behavior of gases.

It will be recalled that Boyle's and Gay Lussac's laws do not exactly describe the behavior of any gas, but that they all vary

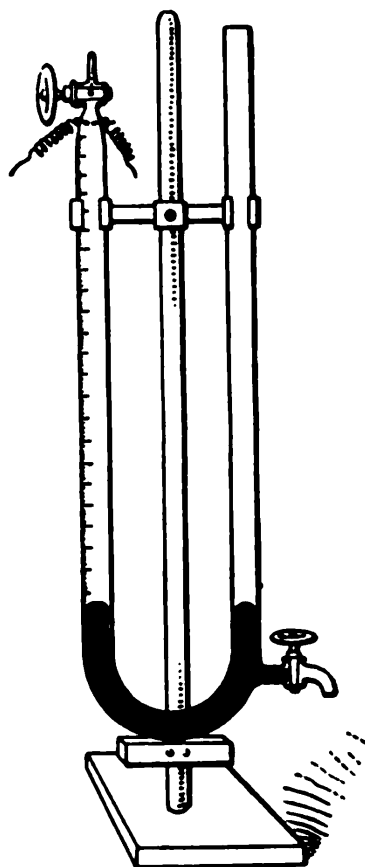


FIG. 18.

somewhat from these. Similarly Gay Lussac's law of combining volumes is not an exact law as may be seen from the fact that hydrogen and oxygen do not combine in the ratio of 2 : 1 as called for by the law, but in the ratio of 2.0025 : 1. The deviations, however, are not large, in most cases, and the law is very useful and important.

**Molar Weight.**—The conception of molar weights which is about to be developed is highly useful since with its aid the interpretation of many apparently complicated chemical phenomena becomes simple.

The molar weight of a gaseous substance is conceived of as being proportional to the density of the gas. For reasons which cannot be brought out until later, the molar weight of oxygen is taken as 32. At the proper point the reasons for this choice will be given. If then the molar weight of a gas is proportional to its density the following relation will hold:

The molar weight of the gas: the molar weight of oxygen = the density of the gas: the density of oxygen, or

$$\frac{\text{The molar weight of the gas}}{\text{The molar weight of oxygen}} = \frac{\text{The density of the gas}}{\text{The density of oxygen}}$$

Substituting for the molar weight of oxygen its value 32, and solving for the molar weight of the gas, we have

$$\text{Molar weight} = 32 \times \frac{\text{The density of the gas}}{\text{The density of oxygen}} = 32 \times \frac{D}{0.001429}$$

where 0.001429 is the density of oxygen and D that of the gas in question.

But  $\frac{D}{0.001429}$  is the specific gravity of the gas referred to oxygen.

Since it is the ratio of the weights of equal volumes (1 c.c. in each case) of the gas and of oxygen. Therefore for a gaseous substance the *molar weight may be defined as thirty-two times the specific gravity of the gas referred to oxygen as the standard.*

For the sake of illustration, let us calculate the molar weight of hydrogen. The density of hydrogen is 0.00008986, and letting M represent the molar weight,

$$M = 32 \times 0.00008986 / 0.001429 = 2.012$$

Therefore the molar weight of hydrogen is 2.012.

Water vapor of course cannot exist under standard conditions,

but could exist at 0°C. if the pressure were less than 0.4 cm. of mercury or at atmospheric pressure if the temperature were higher than 100°C. Since water vapor follows the gas laws, if the weight of a given volume be found under any conditions of temperature and pressure, the density which it would have under standard conditions, if it did not liquefy, can be readily calculated. The density of water vapor obtained in this way is 0.0008063 and hence the

$$\text{Molar weight of water} = 32 \times 0.0008063 / 0.001429 = 18.05.$$

By a slight extension of the conception of molar weight we can get another very useful conception, that of a gram mole. A gram mole of a substance is nothing more or less than the molar weight of the substance expressed in grams. Or it is a weight in grams of the substance numerically equal to its molar weight. For example, the molar weight of hydrogen is 2.012 and a gram mole of hydrogen is 2.012 gm. of hydrogen. The molar weight of water vapor is 18.05, so a gram mole of water vapor is 18.05 gm. of water vapor. The molar weight of oxygen is 32, and a gram mole of oxygen then is 32 gm. of oxygen.

The volume occupied by a gram mole of a gaseous substance under standard conditions can be easily calculated by dividing its molar weight by its density under standard conditions. The volume of a gram mole of oxygen under standard conditions is then  $32 / 0.00143$  or 22,400 c.c. The volume of a gram mole of hydrogen is  $2.012 / 0.00008986 = 22,400$  c.c. These and other examples which may be worked out, together with a few moments thought on the definition of molar weight should soon convince one that the volume of a gram mole of all gases under standard conditions is the same and is 22,400 c.c.

## CHAPTER VI

### COMBINING WEIGHTS AND ATOMIC THEORY

There can be no question but that the law of combining weights is the most important generalization of chemistry, and we must now turn our attention to the formulation of this law. For this, we shall need the composition of a number of compounds as determined by analysis, and their molar weights. In order to obtain accurate results, it is necessary to use not the molar weights directly determined from the gaseous density, but these plus or minus a small experimentally determined number which corrects for the deviations of the gases from the simple gas laws of Boyle and Gay Lussac. These corrections are easily determined and the corrected molar weights are just as much the result of experiment as the uncorrected numbers.<sup>1</sup>

By analysis we get the weight of each element in a gram of the compound. If we multiply the weight of an element in a gram of compound by the molar weight of the latter, we obviously obtain the number of grams of the element per gram mole of the compound. For example a gram of water contains according to analysis 0.8881 grm. of oxygen. The molar weight of water is 18.016. If we multiply these two numbers together, we get 16.00 which means that 18.016 grm. of water contains 16 grm. of oxygen.

The following table summarizes this kind of results for a number of compounds, and should be carefully studied, paying particular attention to the weights of each element per gram mole of compound.

The results given in the following table under the headings, "weight of each element per gram and per gram mole of compound," are as described by the law of definite proportions and

<sup>1</sup> Some idea of the magnitude of these corrections may be obtained by comparing the value for the molar weight of water obtained on p. 69 with the corrected value given in the table p. 71 and also that uncorrected molar weight of hydrogen 2.012 with the corrected 2.016.

each set represents equally well the relative proportions in which the elements unite to form the compounds. The most careful study of the weights of the elements per gram of compound will fail to show any simple relation between the weights of any given element, say hydrogen, in the various compounds; but even a very hasty inspection of the weights of the elements per gram mole shows that a gram mole of a hydrogen compound either contains 1.008 grm. or some integral multiple of this number. The same thing is true for oxygen, nitrogen, etc., except that the number is 16 for oxygen, 14.006 for nitrogen, 35.46 for chlorine, and 12 for carbon.

Name of compound	Weight of each element per gram of compound	Corrected molar weight	Weights of each element per gram mole of compound				
			Hydrogen	Oxygen	Nitrogen	Chlorine	Carbon
Water	0.1119 hydrogen 0.8881 oxygen	18.016	2.016	16.00			
Hydrogen chloride	0.0276 hydrogen 0.9724 chlorine.	36.468	1.008	....	.....	35.46	
Ammonia	0.1776 hydrogen 0.8224 nitrogen	17.030	3.024	....	14.006		
Nitric oxide	0.4668 nitrogen 0.5332 oxygen	30.006	.....	16.00	14.006		
Nitrous oxide	0.6365 nitrogen 0.3635 oxygen	44.012	.....	16.00	28.012		
Carbon dioxide	0.2727 carbon 0.7273 oxygen	44.00	.....	32.00	.....	....	12.00
Minimum weight of each element per gram mole of the compounds.			1.008	16.00	14.006	35.46	12.00

This is true not only for these compounds but also for all other gaseous compounds of these and other elements so that we can make the general statement *that for each element there is a number which represents the minimum weight of that element found per gram mole of any of its compounds, and whenever this element is present in a gram mole of any compound in greater weight than the minimum, its weight may always be represented by an integral multiple of the minimum weight.* These minimum numbers are called the combining weights of the elements because they or their integral multiples represent the proportions by weight in which the elements enter into combination with one

another. The statement just given in italics might be called the law of combining weights, but if preferred the following form may be used. For each element a number can be found which has the property that the proportions by weight in which this element enters into combination with other elements can be represented by this number or some integral multiple of it.

No two elements have the same combining weight and a table of these very important constants is given on p. 79.

**Atomic Theory.**—Just before the beginning of the nineteenth century, the law of definite proportions (p. 27) was formulated, and a few years later John Dalton, an Englishman, discovered some of the facts upon which the law of multiple proportions (p. 84) is based. From a consideration of these relations Dalton became aware of the facts described by the law of combining weights. He also knew the law of the conservation of the elements. As an explanation of all these facts he gave a definite quantitative form to the atomic theory—a theory which had been held by many in some form or other since the days of the early Greek philosophers. For the purpose of explaining the facts, Dalton made the following assumptions:

First, that all elements are made up of very minute chemically indivisible particles called atoms;

Second, that the atoms of any one element are all alike in size, weight, etc., but are very different in all these particulars from the atoms of other elements;

Third, that the ratio of the weights of the atoms of any two elements is the same as the ratio of their combining weights;

Fourth, that compounds are formed by the union of a definite integral number of atoms of one element with a definite whole number of atoms of another to form the smallest particle, called the molecule, of the compound;

Fifth, that the atoms of any given element preserve their identity in passing from the element to a compound, or from compound to compound.

The explanation of the laws upon which the atomic theory is founded in terms of that theory is so simple as to be almost obvious. The fixed relative proportions by weight in which the elements unite to form a given compound (Law of Definite

Proportions) is given by the relative weights of the atoms of the elements, each multiplied by the definite integral number of the atoms of that element which united to form a molecule of the compound. Since the atoms are assumed to be indivisible, it follows that in a molecule of any given compound of an element, there will be one, two, three, or some whole number of atoms of that element; and therefore from the relation between the combining weights and the weights of the atoms, the proportions by weight in which the element enters into combination will be represented by the combining weight or some whole multiple of this (Law of Combining Weights). The law of conservation of elements is explained at once by the assumption that the elements preserve their identity in passing from compound to compound. In terms of the atomic theory, what we have called the combining weights of the elements may just as properly be called the relative atomic weights, or simply the atomic weights of the elements. The table on p. 79 entitled "International Atomic Weights" gives the accepted values of these important constants for the elements.

The atomic theory has proved to be one of the most fruitful theories of chemistry, since it not only explains the very fundamentally important laws of chemical combination, but also has brought together a great many other facts and by predicting new relations has led to investigations which have greatly increased our store of knowledge. For a long time there was no proof that substances were composed of particles the size of atoms and molecules; for all elements and chemical compounds when examined under the most powerful microscopes seemed to be perfectly homogeneous. But within the last few years, facts have come to light chiefly by the study of radioactive substances (see p. 496) which seem to indicate very clearly that such small particles do actually exist, and hence the theory has been greatly strengthened. These facts have even enabled us to make a very close estimate of the number of atoms in a gram combining weight or its synonym—gram atomic weight of any element. This number is  $6.1 \times 10^{23}$  atoms.<sup>1</sup> For example 1.008 grm. of hydrogen or 16 grm. of oxygen will each contain  $6.1 \times 10^{23}$  atoms.

<sup>1</sup>  $6.1 \times 10^{23}$  is an abbreviated way of writing 610,000,000,000,000,000,000.

This almost inconceivably large number of atoms in a comparatively small mass of substance enables us to understand fully why it has never been possible to see the atoms.

**Molecular Theory.**—Just as the atomic theory has proved very useful in explaining the facts of chemical combination, so the molecular theory has been of help in explaining certain of the other facts of chemistry and physics. Among the facts which the theory was devised to explain are those of the behavior of gases, liquids and solids, with changes of pressure and temperature, and also the relations which we have been considering under the conception of molar weights.

The more important assumptions made for the purpose of explaining these facts are:

• First, that every substance is made up of extremely small particles called molecules.

Second, that these molecules in the case of compounds are made up by the union of a definite and whole number of atoms of each of the elements composing the compound; in the case of elements, the molecules may be composed of one or more atoms—usually more than one;

Third, if anything happens to change the number of atoms in a molecule, the nature of the substance is changed;

Fourth, that the molecules behave as though they were exceedingly elastic bodies in a state of rapid and ceaseless motion in all directions, their rates of motion increasing with rise of temperature;

Fifth, because of their rapid motions, the molecules are assumed to occupy only a very small part of the space which is apparently filled by the substance which they constitute. The rest of the space being empty. This dispersion of the molecules is assumed to be especially great in the case of gases, much less for liquids, and generally still less for solids;

Sixth, it is assumed (Avogadro's hypothesis) that equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules.

The pressure exerted by a gas is explained as being due to the hammering of the rapidly moving molecules upon the walls of the containing vessel. The latter part of the fourth assumption will explain the increase in pressure with rising temperature,

if the volume is kept constant; or the increase in volume, if the pressure is unchanged. (Gay Lussac, or Dalton's law.)

Decreasing the volume occupied by a given mass of a gas to one-half its former value will double the number of molecules striking a given area of the wall confining the gas and hence double the pressure. (Boyle's law.)

If Avogadro's hypothesis is true and equal volumes of all gases under the same conditions of temperature and pressure, contain the same number of molecules, then it follows that the weights of these equal volumes will stand to each other in the same ratio as the actual weights of the molecules. We can then by choosing some gas as the standard and assigning to it a certain molecular weight, prepare a system of relative molecular weights of gases which shall have all the properties of that which we have called the molar weights. In fact since oxygen has been taken as the standard and assigned a molecular weight of 32, the numerical values of the molecular weights is just the same as that for molar weights; and a gram mole of a substance is precisely the same quantity of that substance as a gram molecular weight. The expression, molecular weight, is a rather long one, so in accordance with custom, it will generally be replaced in this book by the more convenient word mole.

The same facts of radioactivity (p. 496) which strengthened the atomic theory support the molecular theory and indicate that the number of molecules in a gram molecular weight or gram mole of a substance is the same as the number of atoms in a gram atomic weight—that is to say  $6.1 \times 10^{23}$ . A further strengthening of the molecular theory is furnished by the fact that extremely minute particles, when suspended in a liquid and strongly illuminated, look, when examined by a powerful microscope, like dancing dots of light. The motions of these particles closely correspond in kind and amount to those calculated on the assumption that they are caused by the bombardment of the particles by bodies having the calculated mass and velocity of the assumed molecules.

**Relation Between Fact and Theory.**—In studying a theory we should always be careful to get thoroughly in mind the distinction between the facts, the assumptions and the explanation. The facts are eternally true. The theory is a speculative ex-

planation of the facts in which our imagination has carried us farther than our observations have been able to go. Further observations may show that our imaginings (the theory) was a true picture of the way nature works, or they may bring to light new facts which are so out of harmony with what we had imagined that we have to abandon our former theory and invent an entirely new explanation which shall at the same time cover the old and the new found facts. This last condition has been the usual one in the past and the history of science shows a great pile of discarded theories. Each of these was a good theory in its day because it explained the known facts and thus simplified and coordinated our knowledge and also predicted the existence of other facts and so stimulated investigation with the result that our field of information was greatly extended. Judging from the past we have every reason to expect that the future will replace many of our present theories by better ones. The only difficulty about a false theory is that if it is too firmly believed in, it blinds one to obvious facts and causes others to be misunderstood, and so hinders the progress of science.

The way to use a theory is to keep constantly in mind that it is not a fact and possibly is not true, but to follow up all the lines of investigation which it suggests, always being ready to discover that the facts do not agree with the theory. In particular, one should never hesitate to try a thing which upon other grounds promises success simply because a theory predicts failure.

**Standard of Atomic Weights.**—Our recently acquired knowledge of the number of atoms in a gram atomic weight would enable us to prepare and use a table of the absolute values of the atomic weights instead of that given on p. 79, but these numbers would be long decimal fractions with from 21 to 22 ciphers before the significant figures, and hence would be far less convenient than our present system which like that for molar weight is entirely relative, and therefore necessitates the arbitrary choice of a standard. At first, hydrogen was taken as the standard because it has the smallest combining weight, and was given the relative weight of 1; but of recent years it has been decided that oxygen with a relative weight of 16 is the better standard. One of the principal reasons for this change to oxygen is that many elements

do not form easily volatile compounds so that it is very difficult to determine their combining weights from their minimum weight per gram mole of gaseous compounds. Under these conditions, it is necessary to determine the proportions by weight in which the element of unknown atomic weight will combine with one for which this constant is well known—preferably the standard.

Now hydrogen does not form stable compounds with many of the other elements, while oxygen does. Therefore oxygen is the better for a standard substance. Of course the weight of an element which will combine with 16 gm. of oxygen will not give us directly the atomic weight of the element unless just one atom of it combines with one atom of oxygen; but in any event the weight per 16 gm. of oxygen bears some very simple relation to the atomic weight—*i.e.*, it is twice the atomic weight if two atoms of the unknown combine with one of oxygen, or one-half it if two atoms of oxygen combine with one atom of the other. There is a rather inexact law known as that of Dulong and Petit which states that the product of the atomic weight of a solid element and its specific heat expressed in calories is approximately equal to the constant 6.2. The deviations from this number are rather large, especially for the non-metallic elements of low atomic weight, but in nearly all cases, the value of the atomic weight obtained by determining the specific heat and dividing this into 6.2 is nearly enough correct, so that it will enable us to determine the real value, from the weight which will combine with 16 gm. of oxygen. For example, the specific heat of magnesium is 0.245 and this divided into 6.2 gives 25.3 as the approximate atomic weight of magnesium. But 24.32 gm. of magnesium will combine with 16 gm. of oxygen and therefore the atomic weight of magnesium must be 24.32. For silver the case is a little more complex. The specific heat of silver is 0.057 and this divided into 6.2 gives 109 as the approximate atomic weight of silver. But 215.76 gm. of silver will combine with 16 gm. of oxygen. Since 215.76 is so nearly twice 109, it is evident that in this case two atoms of silver combine with one of oxygen, and that the atomic weight of silver is  $215.76 \frac{1}{2} = 107.88$ . It cannot be too strongly emphasized that these atomic weights are ratio numbers, and that they or their integral multiples represent the proportions by weight in which the elements combine.

**Symbols and Formulas.**—In order to save time and also for the sake of securing a convenient method for the representation of the composition of substances, a system of symbols has been devised which shall at the same time represent the elements and the atomic weights of the elements, and which by combining the symbols of the elements shall represent the compounds, the molecular weights of the compounds and their composition. This system was devised by the celebrated Swedish chemist Berzelius. The symbols for the elements are derived from the names of the elements, using the Latin or Greek word where there is a difference in the name as we pass from language to language. In most cases the symbol is the first letter of the name, for example, the symbols of oxygen and hydrogen are O and H respectively. In case the names of more than one element begin with the same letter, the symbol of the element is formed from this initial letter and a characteristic letter from the name. Take for example chlorine with the symbol Cl. The first letter of the symbol is *always* a capital and the *second* is *always* a small letter. In addition to representing the element one of these symbols also stands for an atomic weight of the element, and so represents a certain number of parts by weight of the element. O stands for oxygen, and 16 parts by weight of oxygen; H for hydrogen, and 1.008 parts by weight of hydrogen; Cl stands for chlorine, and 35.46 parts by weight of chlorine.

Hydrogen and chlorine combine to form hydrogen chloride in the proportion of 1.008 parts by weight of hydrogen to 35.46 parts by weight of chlorine, or of one atomic weight of the one element to one of the other. This is the composition of hydrogen chloride and both hydrogen chloride and its composition can be represented by writing the symbols of the elements close together, viz., HCl. This HCl stands first for hydrogen chloride; second for a mole of hydrogen chloride, that is, 36.468 parts by weight of the substance; third it shows that a mole of hydrogen chloride is formed by the combination of one atomic weight of each of the elements, or of 1.008 parts by weight of hydrogen to 35.46 parts of chlorine. The sum of these atomic weights gives the molecular weight or the parts by weight of the hydrogen chloride represented by the formula HCl.

Water is formed by the union of 2.016 parts by weight of

The formulas of the elements are obtained by applying the principles in the section on Symbols and Formulas. An inspection of the third and fourth columns of the table shows that the atoms of an element are usually not identical with its molecules, but that one of the latter is generally made up by the union of two or more atoms. For example, the molecule of oxygen contains two atoms of oxygen and has a formula of  $O_2$ . At first sight, it might appear that this is due to our choice of oxygen as the standard substance for both atomic and molecular weights, and arbitrarily giving it an atomic weight of 16 and a molecular weight of 32; and that if we had called it 16 in each case, that the atom and the molecule would have been identical. But the following reasoning will show that the atom cannot be the same as the molecule. Hydrogen and oxygen combine to form water in the proportion of two volumes of hydrogen to one of oxygen, (see p. 67) forming two volumes of water vapor. If we take as the unit of volume the volume of one gram mole—22,400 c.c. under standard conditions—we will have the following volume and weight relations:

$2 \times 22,400$  c.c. of hydrogen + 22,400 c.c. oxygen =  $2 \times 22,400$  c.c. water vapor.

$2 \times 2.016$  gram. of hydrogen + 32 gram. oxygen =  $2 \times 18.016$  gram. water vapor.

Then 2 gram. moles of hydrogen react with 1 gram. mole of oxygen to form 2 gram moles of water vapor; but each gram mole of a substance on the basis of Avogadro's hypothesis contains the same number of molecules. Therefore there are just twice as many molecules of water as there are molecules of oxygen. The assumed indivisibility of atoms makes it impossible to assume that a molecule of water contains less than one atom of oxygen; hence if a molecule of water contains one atom of oxygen, a molecule of oxygen must contain two atoms. Therefore if the atomic weight of oxygen is taken as 16, its molecular weight *must* be 32. This then is the basis for the apparently arbitrary choice of 32 as the molar weight of oxygen (p. 68).

**Chemical Equations.**—As was said above, two atomic weights of hydrogen unite with one of oxygen to form a mole of water; this can be very well shown with the aid of symbols as follows;



and this is an example of a chemical equation. A chemical equation is a very simple shorthand method of representing a chemical reaction quantitatively. For example, the above equation shows that 2.016 parts by weight of hydrogen will combine with 16 parts by weight of oxygen to form 18.016 parts by weight of water. The unit of weight may be the gram, pound or any other weight unit, and the equation will hold just the same.

We have learned that two volumes of hydrogen will combine with one volume of oxygen to form two volumes of water vapor, or two moles of hydrogen and one mole of oxygen will give two moles of water vapor. In representing this we shall have to use the molecular formulas for everything. Now the molecular weights of hydrogen and of oxygen are twice their atomic weights so their molecular formulas are  $H_2$  and  $O_2$  respectively. We may show that two moles of hydrogen combine with one of oxygen thus,



This is read "two moles of hydrogen combine with one mole of oxygen to give two moles of water vapor." The coefficients or numbers before the formulas show the number of moles taking part in the reaction, while the subscripts show the number of atomic weights of that element per mole. The coefficients therefore multiply every symbol in the formula which they stand before, as for example,  $2H_2O$  represents 2 moles of water of  $2 \times 2$  atomic weights of hydrogen and  $2 \times 1$  atomic weights of oxygen. On either side of the above equation there are represented then, four atomic weights of hydrogen and two of oxygen. This is the proof that the equation is properly "balanced." There are two main principles involved in writing these equations. First, the formulas separated by  $+$  should be molecular formulas, and second, there must be the same number of atomic weights of any given element on either side of the equation, since otherwise we would be indicating a deviation from the law of the conservation of weight. The advantage of writing molecular formulas lies in the fact that since gram moles of gases occupy equal volumes under like conditions we can tell at once their proportion by volume, from a simple inspection of the number

of moles of the one that reacts with the other. The proportions by volume in which gases react are given by the coefficients in the molecular equation for the reaction.

When one of these equations is first worked out, it must be found by experiment just what things are formed by the substances which react and the proportions by weight of everything involved in the process. There is no other way of doing it. We must know what is brought together and what is formed before we can represent it by symbols. Students often think that they fail to grasp the idea of equations because they cannot write down symbols and formulas for a number of substances on one side of the equation and then tell by some rule what to put on the other, or else they jump to the other extreme and think that the symbols can be combined in any way at the fancy of the writer. But the truth of the matter is that only certain substances are formed from certain other ones, and one must know what these are and then represent them. Every equation then represents the results of actual experiment. It will be recalled that water and sodium react and form sodium hydroxide and hydrogen. The sodium hydroxide contains per mole 23 parts by weight of sodium, 16 of oxygen, and 1.008 of hydrogen. Its formula then is NaOH and the molecular weight is a little over 40. We find by experiment that when 36.032 gm. of water react on 46 gm. of sodium that 2.016 gm. of hydrogen and 80.016 gm. of sodium hydroxide are formed. We may represent this by the following equation,



In studying the properties of substances it is very essential to learn with what other substances they will react and the substances formed. It is not necessary to learn in what proportions they react as, given the other information, the proportions can be reasoned out from the rules for balancing which were given above.

Knowing the substances and their weights we can write the equation, or given the equation we can work out the weights from the atomic weights.

## CHAPTER VII

### HYDROGEN PEROXIDE

Hydrogen and oxygen will combine in the ratio of one part by weight of hydrogen to 7.943 parts by weight of oxygen, and in no other ratio when they unite to form water. However, they will combine in a different proportion for the formation of an entirely distinct substance known as hydrogen peroxide. The ratio in this case is one part by weight of hydrogen to 15.886 parts by weight of oxygen. If we now compare the parts by weight of the oxygen in the two compounds which will combine with one part of hydrogen we see that they stand to each other as 1 : 2

$$7.943 : 15.886 = 1 : 2$$

This is the first time that we have found a really simple weight relationship and this you will notice is the ratio between the weights of the one element which will combine with unit weight of the other element in the two compounds. This sort of a simple weight relation has been found to be so common that a law has been formulated to describe it.

**The Law of Multiple Proportions.**—*If two elements, which we may represent by A and B, combine to form more than one compound then the number of grams of A which combine with one gram of B in the first compound will stand to the number of grams of A per gram of B in each of the other compounds in the proportions of whole numbers and usually these numbers are small ones.*

Hydrogen and oxygen always combine in one fixed ratio for the formation of water, and in another equally fixed for the formation of hydrogen peroxide, so the law of definite proportions describes the composition of each of these compounds and the law of multiple proportions applies to the two taken together.

**Preparation and Properties of Hydrogen Peroxide.**—Hydrogen peroxide is prepared in a number of ways, but the greater part of that used is made by the action of dilute sulfuric acid upon hydrated barium peroxide, barium sulfate being formed at the

same time. It is not practical to prepare it directly from the elements although minute quantities are formed by allowing the flame of an oxy-hydrogen blowpipe to play upon ice. The hydrogen peroxide prepared by the interaction of barium peroxide and sulfuric acid is present in a dilute solution with water. To prepare pure hydrogen peroxide is not easy, but the method usually adopted depends upon the fact that hydrogen peroxide is less volatile than water, so that if a mixture of the two be distilled, relatively more of the water than of the hydrogen peroxide will pass off, and the residue will contain more and more hydrogen peroxide per cubic centimeter. By repeating the process, nearly pure hydrogen peroxide may be obtained. Hydrogen peroxide is rather unstable and decomposes into water and oxygen. This reaction like nearly all others goes more rapidly at high temperatures than at lower ones, therefore the process of distillation is carried out under diminished pressure because this lowers the boiling-point.

Hydrogen peroxide is a rather thick, syrupy liquid which has a very faint greenish-blue color somewhat more intense than that of water. Its density at 0°C. is 1.46. It melts at  $-2^{\circ}$  and boils at  $69^{\circ}$  under a pressure of 2.6 cm. of mercury. Its boiling-point under atmospheric pressure is not known as it decomposes with explosion before it boils. It is odorless and has an astringent bitter taste. It is soluble in water in all proportions and the solution looks like water. This solution slowly decomposes into water and oxygen and keeps best in the dark, in a cool place, and when it contains a little acid. This transformation seems especially sensitive to the presence of foreign substances which after the completion of the process are found unchanged. These substances are therefore catalyzers. The following is a partial list of the catalyzers of the decomposition of hydrogen peroxide; charcoal, silver, gold, platinum, manganese dioxide, potassium and sodium hydroxides, saliva, and blood. The solid substances mentioned act the more vigorously the finer they are powdered.

A 3 per cent. solution is a standard article of commerce. It is often called a 10-volume solution from the fact that it will evolve, when all the hydrogen peroxide is decomposed, about ten times its volume of oxygen. This solution will rapidly destroy bacteria, and hence is much used as a disinfectant.

**Oxidizing Action of Hydrogen Peroxide.**—Since hydrogen peroxide gives up part of its oxygen so easily that it will do it even at ordinary temperatures, it seems very natural to expect that it will be able to give it up to other things which can combine with oxygen and thus oxidize them. Upon trial this is found to be the case, and this action is exhibited more strongly as the hydrogen peroxide becomes more concentrated; that is, the greater the weight of this substance per cubic centimeter. If the pure hydrogen peroxide be brought in contact with many inflammable substances, the latter are oxidized so rapidly that they ignite spontaneously. The solutions are much less intense in their action and decrease in activity as the dilution is increased.

Substances which will give up oxygen to other substances in the way that hydrogen peroxide does are called oxidizing agents. As we shall see later, oxidizing agents can do many things besides give up oxygen to other substances, but this is one of the things which they may do, and must be kept in mind until finally we come to a definition of an oxidizing agent which will cover all cases. Other oxidizing agents are like hydrogen peroxide, in that they act more vigorously as their concentration increases. Because of its action as an oxidizing agent, hydrogen peroxide is able to change many organic coloring matters into colorless substances, and it is therefore used for bleaching hair, feathers, ivory, silk, wool, bones, leather, etc. For this purpose fairly dilute solutions are used.

**Reducing Action of Hydrogen Peroxide.**—When hydrogen peroxide acts upon many oxides such as those of silver, gold and mercury, the metals, water and oxygen are produced. The process of obtaining a metal from its oxide is an example of reduction, and hence hydrogen peroxide acts in these cases as a reducing agent. Potassium permanganate is also reduced by hydrogen peroxide and in this case again oxygen is evolved.

**Determination of the Molecular Weight of Hydrogen Peroxide.**—Hydrogen peroxide is so unstable that it is not possible to determine its molecular weight from its gaseous density, but recourse must be had to an entirely different method called the "Freezing-point Method."

It will be recalled that mention has been made of the fact

that any dissolved substance lowers the freezing-point of water, and also that gram moles of the various substances produce equal physical effects. Experiment has shown that if a gram mole of substance be dissolved in 1,000 grm. of water, the freezing-point of the water is lowered  $1.85^{\circ}\text{C}$ . This then furnishes a ready method for the determination of the molecular weight of such substances as hydrogen peroxide which cannot be vaporized without decomposition. The molecular weight of a substance, with some exceptions, as noted below, is identical with the number of grams of the substance required to lower the freezing-point of 1,000 grm. of water  $1.85^{\circ}\text{C}$ .

Any convenient weight of the solute and of water may be used and the molecular weight of the solute calculated from the equation,

$$M = 1,850 \frac{w}{LW}$$

in which "M" represents the molecular weight of the solute, "w" the weight of the solute, "W" the weight of the water, "L" the lowering of the freezing-point.

The molecular weight of hydrogen peroxide determined in this way comes out close to 34.

Under the discussion of water it was pointed out that solutes lowered the vapor pressure of their solvents and that there was a connection between this fact and the fact that the solutions froze at lower and boiled at higher temperature than their pure solvents. From these facts, one would be led to expect that there would be a constant rise in the boiling-point of water per gram mole of solute per 1,000 grm. of water, because gram moles are in the main, physically equivalent. This is found to be the case. One gram mole of a substance with the exceptions noted below will raise the boiling-point of 1,000 grm. of water  $0.52^{\circ}\text{C}$ ., and a method for the determination of molecular weights is based upon this. The formula is

$$M = \frac{520w}{rW}$$

in which M, w, and W have the same significance as before, and "r" is the rise in the boiling-point, and 520 the proportionality constant.

As has been implied above, there are some exceptions to the rule that a gram mole will lower the freezing-point of 1,000 grm. of water 1.85°C or raise the boiling point 0.52°C. We will find later that these exceptions lead to very interesting and important conclusions. All these exceptional substances yield solutions which are conductors of electricity. Hydrogen peroxide in solution is a non-conductor, so we may feel confident that the molecular weight given above is correct.

**Composition and Formula of Hydrogen Peroxide.**—Before the formula of any compound can be worked out the substance must be analyzed or synthesized and its molar weight determined. From the data the formula is then made up in a way which may be well illustrated by hydrogen peroxide.

The analysis of hydrogen peroxide shows that it consists of 5.93 per cent. hydrogen and 94.07 per cent. oxygen.

From these data and its molecular weight 34.016, it is a simple matter to calculate the number of parts by weight of each element per mole of the peroxide as follows:

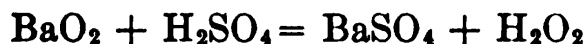
$$\frac{34.016 \times 5.93}{100} = 2.016 \text{ parts by weight of hydrogen}$$

and

$$\frac{34.016 \times 94.07}{100} = 32.0 \text{ parts by weight of oxygen.}$$

Since the atomic weight of hydrogen is 1.008 and of oxygen is 16, it is evident at a glance that there is in a mole of hydrogen peroxide two atomic weights of hydrogen and two of oxygen and therefore its formula is  $\text{H}_2\text{O}_2$ .

**Equation for the Preparation of Hydrogen Peroxide.**—As has been already mentioned, hydrogen peroxide may be prepared by the action of dilute sulfuric acid upon barium peroxide, barium sulfate being formed at the same time. The equation for the reaction is as follows:



in which  $\text{BaO}_2$  stands for 169.37 parts by weight of barium peroxide,  $\text{H}_2\text{SO}_4$  for 98.076 parts by weight of sulfuric acid,  $\text{BaSO}_4$  for 233.43 parts by weight of barium sulfate, and  $\text{H}_2\text{O}_2$  for 34.016 parts by weight of hydrogen peroxide.

**Explosive Properties of Hydrogen Peroxide.**—Pure or nearly pure hydrogen peroxide is decidedly explosive. The explanation for this is that the peroxide passes into water and oxygen with the evolution of a great amount of heat, so that if decomposition gets started, the heat evolved raises the temperature of the remaining peroxide and this makes it break up more rapidly, evolving still more heat and raising the temperature yet higher, thus making it decompose even faster until the reaction takes place so violently that it is explosive. All other explosives are like hydrogen peroxide in that they give off heat during their transformation, and in fact they owe their explosiveness to this property.

Explosives are rather unusual substances because most things decompose with the absorption of heat, and hence if they once start to decompose they cool themselves off and so tend to stop the action. So pronounced is the heat of decomposition of hydrogen peroxide that even the dilute solution of commerce will experience a rise in temperature of 15° to 20°C. upon the addition of manganese dioxide which will catalytically bring about a rapid destruction of the peroxide.

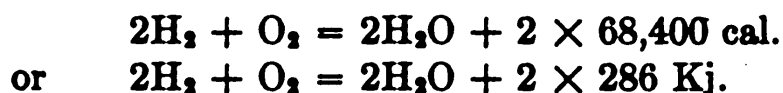
**Thermochemistry.**—Practically every chemical change is accompanied by either the absorption or evolution of heat. These heat effects are of importance because, if the conditions are made such that no work is done, they represent the difference in energy between the substances before and after the reaction. These differences in energy are of vital importance to us because it is really the difference in energy between the coal and oxygen on the one hand and the products of combustion on the other which drives the steam engine, cooks our food, and keeps us warm.

These heat effects are measured in very much the same way as the heat of fusion of ice or the heat of evaporation of water, and are expressed in calories or kilojoules per gram, or better still per gram mole of substance transformed.

By a very slight addition to our scheme for representing chemical reactions we can indicate at the same time the chemical and energy changes. In doing this the chemical formulas stand for gram moles of the various substances, and at the end of the equation is written the number of kilojoules "Kj" or calories

evolved or absorbed, evolution being indicated by a plus (+) sign and absorption by a minus (-).

To illustrate this, let us consider the heat effect accompanying the burning of hydrogen to form water. For every gram mole of water produced 68,400 calories or 286 kilojoules of heat are evolved. This is represented as follows:



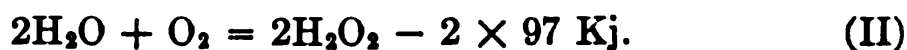
The heat effect accompanying the formation of a gram mole of a substance is called its **heat of formation**, so the heat of formation of water is 286 Kj. or 68,400 cal. per mole.

There are two points in connection with thermochemical equations such as those just given, which must be carefully kept in mind. The first one is—that if a certain quantity of heat is evolved during the formation of a gram mole of a substance, precisely the same quantity of heat will be taken up during its decomposition. The second is that the heat effect accompanying a given transformation depends only upon the initial and final states of the substances and not at all upon the intermediate stages through which they pass.

**The Heat of Formation of Hydrogen Peroxide.**—Since hydrogen and oxygen combine with such difficulty to produce hydrogen peroxide it is not possible to determine the heat of formation of this substance by direct measurement. This magnitude may, however, be calculated by taking advantage of the facts pointed out above. Hydrogen peroxide spontaneously decomposes into water and oxygen, and the heat effect belonging with this change may be easily measured. It is 97 Kj. or 23,100 cal. per mole of peroxide transformed. The equation is

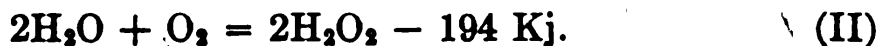


From what has been said above and the law of the conservation of energy, it follows that if oxygen and water should unite to form hydrogen peroxide that 97 Kj. of heat would be absorbed for each gram mole of peroxide formed, the equation being



The heat of formation of the peroxide from oxygen and water

therefore is  $-97$  Kj. To obtain the heat of formation from the elements, all that is necessary is to add to the above number the heat of formation of the water. In fact these thermochemical equations may be handled like ordinary algebraical equations. To equation (II) may be added the equation for the formation of water and the result will be the equation for the formation of the peroxide from its elements.



or



So the heat of formation of hydrogen peroxide is  $189$  Kj. or  $45,300$  cal. per gram mole. Of course the thermochemical equations expressed in cal. may be substituted for those in Kj. and the figure  $45,300$  will then be obtained directly.

The method applied here is a general one for calculating the heat effects which cannot be directly measured.

## CHAPTER VIII

### CHLORINE

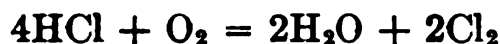
The third element which we will discuss is chlorine. This element does not occur free in nature but is found in very large quantities in compounds, such as sodium, potassium, and magnesium chlorides. The element itself and many of its compounds are of very great importance not only in the chemical industries, but also in every-day life. The sodium chloride,  $\text{NaCl}$  for example, is our common salt, and we all know how indispensable this is. Sodium chloride is found in enormous quantities in beds of rock salt at many places on the earth's surface and is present in still larger quantities in the ocean.

Chlorine was first prepared by Scheele in 1774, but that it was an element was first shown by Sir Humphrey Davy in 1810.

**Preparation of the Element.**—There are a few chlorides, such as those of gold and platinum, which will decompose into chlorine and the metals upon being raised to a high temperature, but these chlorides are so expensive and difficult to make that chlorine is practically never prepared in this way. The preparation of chlorine, then, resembles that of hydrogen more nearly than that of oxygen, in that a compound of chlorine is treated with some substance which will convert the rest of the chlorine compound into a substance which will readily take on a different physical state from that of the gaseous chlorine and hence may be easily separated from this element. Chlorine may also be liberated by electrolysis of solutions of soluble chlorides very much as hydrogen and oxygen may be prepared. In the case of the electrolysis of the chlorides, chlorine is given off at one electrode, and either hydrogen or the metal of the chloride is deposited at the other.

The most suitable substance for the chemical preparation of chlorine seems to be hydrochloric acid, a compound of chlorine and hydrogen whose formula is  $\text{HCl}$ . From this hydrogen chloride or hydrochloric acid, we can easily prepare chlorine by

converting the hydrogen into water. This may be done in several ways. Gaseous hydrogen chloride mixed with oxygen or air may be passed through a tube containing clay balls or pieces of pumice stone coated with copper chloride or sulfate, heated to  $370^{\circ}$  to  $400^{\circ}\text{C}$ . Under these conditions water and chlorine are produced according to the equation,



The copper salt acts as a catalyzer.

When air is used the product is of course greatly contaminated with nitrogen, as well as unchanged hydrogen chloride and oxygen, so that the method is not suitable for laboratory purposes, but was formerly largely used for the commercial preparation of chlorine, and is known as the Deacon Process.

**Other Methods.**—The preparation of chlorine from hydrogen chloride belongs to the processes which we call oxidation, and

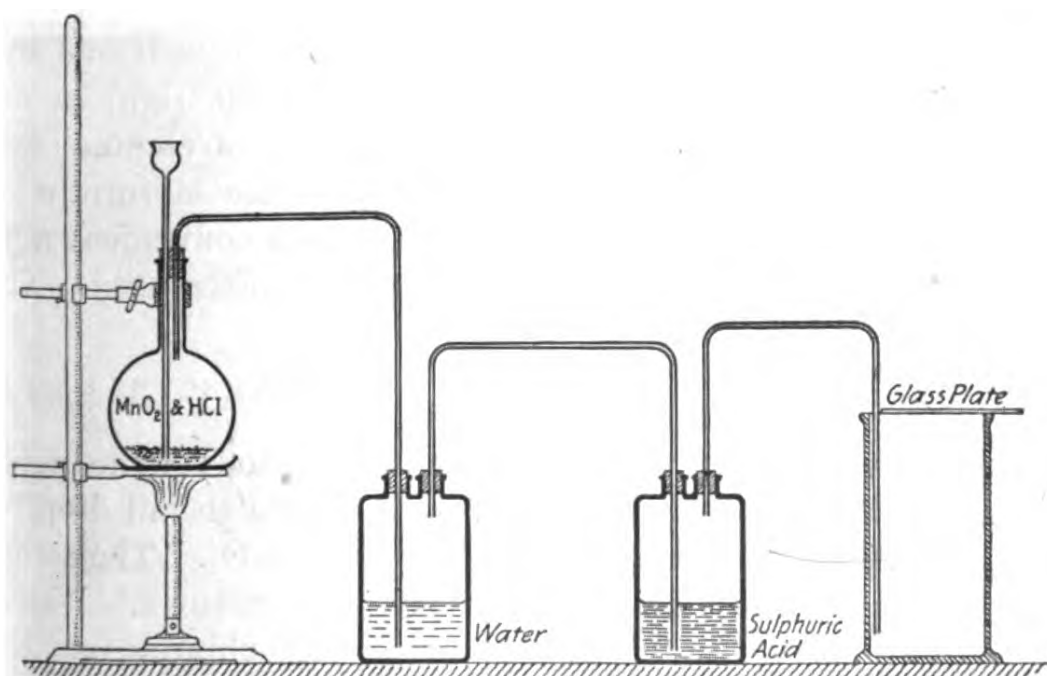


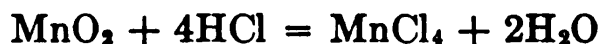
FIG. 19.

oxygen here is the oxidizing agent. Other oxidizing agents, if sufficiently powerful, may be used in the place of oxygen. Among those which are convenient may be mentioned manganese dioxide,  $\text{MnO}_2$ , potassium chlorate,  $\text{KClO}_3$ , potassium permanganate,  $\text{KMnO}_4$ , and bleaching powder,  $\text{CaCl}_2\text{O}$ . Each of these substances when treated with hydrochloric acid will oxidize the latter to water and chlorine.

A very commonly used laboratory method for the preparation of chlorine is to gently heat a mixture of manganese dioxide with four times its weight of commercial hydrochloric acid (Fig. 19). The liquid first turns brown and then gives off greenish-yellow gaseous chlorine. After the reaction is finished, the solution contains manganous chloride,  $\text{MnCl}_2$ . The equation is



It seems to be very probable that the reaction goes in two stages, first forming water and manganese tetrachloride,  $\text{MnCl}_4$ , which is dark colored, and then this tetrachloride decomposes into the lighter colored manganous chloride,  $\text{MnCl}_2$ , and chlorine,  $\text{Cl}_2$ . The equations representing this would be



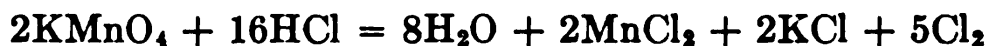
and



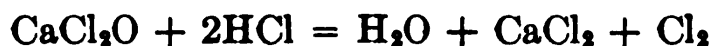
Instead of starting with hydrochloric acid and manganese dioxide one may form the hydrochloric acid from salt and sulfuric acid and oxidize it with manganese dioxide right in the same vessel. To do this one warms a mixture of common salt and manganese dioxide with moderately dilute sulfuric acid. The chlorine comes off very regularly, and at a convenient rate, so that this modification of the first method is often used. The equation is



Perhaps the most convenient laboratory method for the preparation of chlorine is to allow hydrochloric acid to fall drop by drop upon solid potassium permanganate,  $\text{KMnO}_4$ . The action takes place promptly and at ordinary temperatures. Water, manganous chloride, potassium chloride, and chlorine are the products. The equation is



A very important method which is much used both in the laboratory and technically is to treat bleaching powder,  $\text{CaCl}_2\text{O}$ , with hydrochloric acid. Water, calcium chloride,  $\text{CaCl}_2$ , and chlorine are the products. The equation is



*It should be noted that in each of the above cases liquid water, a non-volatile salt or salts, and gaseous chlorine are formed. This difference of state makes it easy to isolate the chlorine.*

**Technical Preparation.**—Each of the above-mentioned methods for the preparation of chlorine, together with many others, has been used on a manufacturing scale, but at the present time the greater part of the chlorine of commerce is produced by the electrolysis of solutions of sodium or potassium chloride see Fig. 52, p. 281. The anode or positive electrode where the chlorine appears is usually made of graphite because almost everything else is attacked by the chlorine. At the cathode or negative electrode hydrogen is given off and sodium or potassium hydroxide is formed in solution. The process takes place as though metallic sodium or potassium were liberated at the cathode and then at once reacted with the water for the formation of hydrogen and sodium or potassium hydroxide.

**Physical Properties.**—At ordinary temperatures chlorine is a greenish-yellow gaseous substance whose density is 0.0032215 and whose uncorrected molecular weight is 72.13. Chlorine does not follow the gas laws very closely, a fact which is connected with the circumstance that it is very easily converted into a liquid either by cooling it to  $-33.6^{\circ}\text{C}$ . under a pressure of one atmosphere, or by putting it under a pressure of 3.66 atmospheres at  $0^{\circ}\text{C}$ . or of 6.62 atmospheres at  $20^{\circ}\text{C}$ . The critical temperature is  $146^{\circ}$  and the critical pressure 94 atmospheres. After correcting for its deviations from the gas laws the molecular weight of chlorine is found to be 70.92.

Liquid chlorine has a greenish-yellow color, a density of 1.56, and is of an oily consistency. At  $-102^{\circ}$  the liquid freezes to yellow crystals of solid chlorine.

Gaseous chlorine is soluble in about half its volume of cold water but is much less soluble in hot. Because of its solubility in cold water and the fact that it attacks mercury with great vigor, chlorine must be collected over hot water or by displacement of air. The latter is the more convenient, and since chlorine is nearly 2.5 times as heavy as air, it is easily carried out.

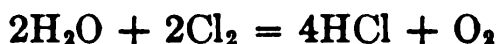
Chlorine has a very disagreeable odor, is exceedingly irritating to the mucous membrane of the throat and nose and has often produced death.

**Chemical Properties.**—The atomic weight of chlorine is 35.46 and its corrected molecular weight is twice this, so there are two atomic weights per mole and the formula is  $\text{Cl}_2$ . Chlorine is a rather more active element than oxygen and combines with almost all the other elements to form compounds called chlorides. In many cases the combination takes place with the production of light and heat, and closely resembles the combustion of substances in oxygen. So striking is the resemblance that we call the phenomena combustion in chlorine. In fact chlorine reacts so vigorously with a number of other substances that they will take fire spontaneously when introduced in the gas at ordinary temperatures. Among these may be mentioned thin copper foil, phosphorus, and powdered antimony. In each case a chloride is formed.

When completely dry, chlorine is much less active than when moist, and carefully dried liquid chlorine is now an article of commerce, being sold in strong steel cylinders lined with lead or bronze. One of the most important chemical properties of chlorine is that it is able to destroy many coloring substances, and it is therefore extensively used as a bleaching agent in the cotton and paper industries. It bleaches only in the presence of water, and is not able to destroy many of the mineral dyes nor black tints due to carbon in the form of lamp black. Chlorine makes all animal fibers very weak and therefore cannot be used to bleach wool or silk.

It is a very powerful disinfectant and is much used to destroy bacteria.

**Chlorine Water.**—As has been mentioned, chlorine is fairly soluble in water. The solution, which has the greenish-yellow color, the odor, and taste, and bleaching qualities of the gas is called chlorine water. A portion of the gas undergoes a chemical change with the water, forming compounds which can best be discussed later. When exposed to sunlight, the chlorine disappears, oxygen is given off, and hydrochloric acid is left. The equation is



This reaction appears to be just the reverse of that taking place in the Deacon Process, but there is this difference that the

Deacon Process takes place in the gaseous state, while this goes on in dilute solution; and under these circumstances the hydrochloric acid and oxygen are more stable than chlorine and water.

The action of chlorine upon water takes place slowly in the dark but much more rapidly in the light, and the more rapidly the stronger the light. The different kinds of light act quite differently; the red rays are almost without effect while the blue, violet and ultra-violet rays are especially active. This action of light is an example of what is known as photo-chemical action.

**Chlorine Hydrate.**—When chlorine is passed into ice-cold water, there soon separates out a greenish crystalline substance which is a compound of water and chlorine having the formula  $\text{Cl}_2 \cdot 8\text{H}_2\text{O}$  and is called chlorine hydrate. It is a rather unstable compound breaking down at room temperature into chlorine and water.

Chlorine hydrate is now being prepared on a large scale as one of the steps in the process of manufacturing liquid chlorine from the impure gas obtained by the electrolysis of sodium or potassium chlorides. The chlorine is cooled to a low temperature and exposed to the action of a spray of cold water. The hydrate is formed thus removing the greater part of the chlorine from the gaseous mixture. The hydrate decomposes at higher temperature into water and chlorine, the latter is dried and is then practically pure and ready for liquefaction.

**The Naming of Chlorides.**—As has been mentioned, the compounds of other elements with chlorine are usually called chlorides, prefixing the name of the other element to form the name of the compound, as for example—sodium chloride, potassium chloride, etc. If, as is not infrequently the case, the same element will form more than one compound with chlorine, it becomes necessary to distinguish between these substances. Where there are only two of these compounds, they are commonly distinguished by adding to the name of the element other than the chlorine the terminations -ous and -ic. The -ous being used for the compound containing the smaller and the -ic for that containing the larger amount of chlorine per combining weight of the other element. There are two chlorides of iron, the one  $\text{FeCl}_2$  is called ferrous

chloride, and the other  $\text{FeCl}_3$  is called ferric chloride. Similarly we have mercurous chloride  $\text{HgCl}$  and mercuric chloride  $\text{HgCl}_2$ . In some cases, particularly where there are more than two compounds of an element with chlorine, the necessary distinction is made by prefixing to the chloride the Greek word signifying the number of combining weights of chlorine to a combining weight of the other element. For example we have phosphorus trichloride,  $\text{PCl}_3$ , and phosphorus pentachloride,  $\text{PCl}_5$ . This same system of nomenclature is applied in distinguishing between the compounds in other cases in which the same pair of elements unite in different proportions to form more than one compound. For example, in the case of the oxides we have mercurous oxide,  $\text{Hg}_2\text{O}$ ; mercuric oxide,  $\text{HgO}$ ; ferrous oxide,  $\text{FeO}$ ; ferric oxide,  $\text{Fe}_2\text{O}_3$ ; sulphur dioxide,  $\text{SO}_2$  and sulphur trioxide,  $\text{SO}_3$ .

**Hydrogen Chloride.**—Hydrogen chloride is an exceedingly important compound of chlorine. It may be formed by the direct combination of the two elements, which can be brought about in a number of ways most of which closely resemble those which will induce the combination of hydrogen and oxygen. For example, a stream of hydrogen will burn in an atmosphere of chlorine much as in air except that the color of the flame will be a peculiar green instead of the blue of the ordinary flame. A colorless gaseous compound is formed which fumes when brought in contact with the air. This is hydrogen chloride. It is much more readily soluble in water than chlorine, does not bleach as chlorine does, but turns blue litmus red. Its solution in water does not in any way resemble chlorine water, but is highly acid and is identical with hydrochloric acid, of which we have had much to say. It has an odor which is disagreeable, but entirely different from that of chlorine. It has a very sour taste, like all other acids, and in this respect also it differs materially from chlorine. In fact hydrogen chloride is unlike chlorine in color, odor, taste, solubility, action on colors, and in every other property, both physical and chemical.

Another method for bringing about the combination of hydrogen and chlorine is to mix the gases and pass an electric spark through a portion of the mixture. As was the case when this was done with a mixture of hydrogen and oxygen, the gases at once combine, with a violent explosion. If equal volumes of hydrogen

and chlorine are used, both of the gases entirely disappear, and the volume of the hydrogen chloride produced is equal to the sum of the volumes of the separate gases. This shows that the combination follows Gay Lussac's law of combining volumes. If an excess of either gas is used, that excess is left uncombined. The equation for the reaction is



which shows that one mole of hydrogen, 2.016 parts by weight of hydrogen, will combine with one mole of chlorine, 70.92 parts by weight of chlorine to form two moles of hydrogen chloride, or  $2 \times 36.468$  parts by weight of hydrogen chloride. The composition of hydrogen chloride is 1.008 parts by weight of hydrogen to 35.46 parts by weight of chlorine, or 2.76 per cent. hydrogen and 97.24 per cent. chlorine.

If the mixed gases be heated to a temperature of between  $240^\circ$  and  $270^\circ\text{C}$ . explosion takes place. Hydrogen and oxygen, it will be recalled, behave in much the same way except that the combination takes place at a higher temperature.

There is one method for bringing about the combination of hydrogen and chlorine which entirely fails in the case of hydrogen and oxygen. This is with light. A mixture of hydrogen and chlorine combines very slowly in absolute darkness. If the mixture be exposed to light, the combination takes place at a rate which can be measured and which is proportional to the intensity of the light. In ordinary diffused daylight the reaction is complete in a few days, while if the mixture be exposed to full sunlight or to the light of burning magnesium, explosion almost instantly results.

**Photochemical Action.**—The action of light in accelerating the union of hydrogen and chlorine is another example of photochemical action. In this case the light certainly does not have to impart energy to the mixture, because the combination takes place even in the dark and always with a very great decrease in the energy so that a large amount of heat is evolved. A completely dry mixture of chlorine and hydrogen is insensitive to light, so water plays an important part in the process.

**Action of Chlorine on Hydrogen Compounds.**—Oxygen, it will be recalled, was able to act upon many compounds of hydrogen in

such a way as to produce water. Similarly, chlorine will react with hydrogen compounds for the formation of hydrogen chloride. We have had an example of this in the case of chlorine and water. A still more striking case is that of chlorine and turpentine. Turpentine is a compound of hydrogen and carbon  $C_{10}H_{16}$ . If a piece of filter paper be dipped into some slightly warmed turpentine and then introduced into a cylinder of chlorine (Fig. 20, *a*), the latter will combine with the hydrogen of the turpentine with the production of so much heat that after a moment the turpentine bursts into a dark red flame which deposits all the carbon in the form of soot, and forms hydrogen chloride which may be identified by its properties. Paraffine is composed of compounds of hydrogen and carbon, and when a burning paraffine candle (Fig. 20, *b*) is introduced into chlorine, it continues to burn, but with a darkened flame and the formation

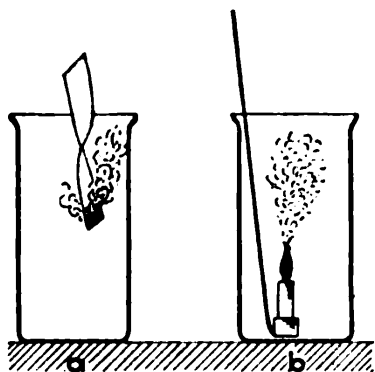


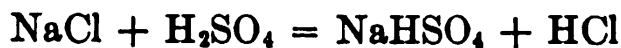
FIG. 20.

of hydrogen chloride and of soot, because under these circumstances chlorine does not combine with carbon.

When natural gas is mixed with chlorine and exposed to sunlight, the methane,  $CH_4$ , which is the chief constituent of the gas, is attacked and hydrogen chloride, together with a number of chlorine substitution products of methane are formed.

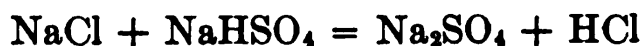
The first of these products is methyl chloride,  $CH_3Cl$ , and the final one is carbon tetrachloride,  $CCl_4$ . These actions take place slowly and at ordinary temperatures.

**Laboratory and Technical Preparation of Hydrogen Chloride.**—The methods previously given are not suitable for the preparation of any considerable quantity of hydrogen chloride. It therefore is almost invariably prepared by acting upon common salt—sodium chloride—with sulfuric acid. This action goes on in two stages. The first takes place at very moderate temperatures and consists in acting upon one mole of sodium chloride with one mole of sulfuric acid to form a mole of sodium acid sulfate and one of hydrogen chloride as shown in the equation



At a considerably higher temperature the second stage takes

place and consists in acting upon a mole of sodium chloride with a mole of sodium acid sulfate to form a mole of neutral sodium sulfate and one of hydrogen chloride,



These two equations may be added together to obtain one which will represent the complete process



The operation is carried out in the laboratory in a glass flask, (Fig. 21) and the temperature cannot be raised high enough to carry it beyond the first stage. On a manufacturing scale the process is carried through the first stage in a large iron pan, A, heated from below (Fig. 22), covered with a brickwork dome, B, covered with a brickwork dome; and finished in a fire clay muffle, B. Both dome and muffle are connected by a flue with brick towers filled with coke over which a small stream of water is kept trickling. The hydrochloric acid vapors pass up through the towers against the stream of water and are absorbed. Almost saturated hydrochloric acid runs out from the bottom of the first tower.

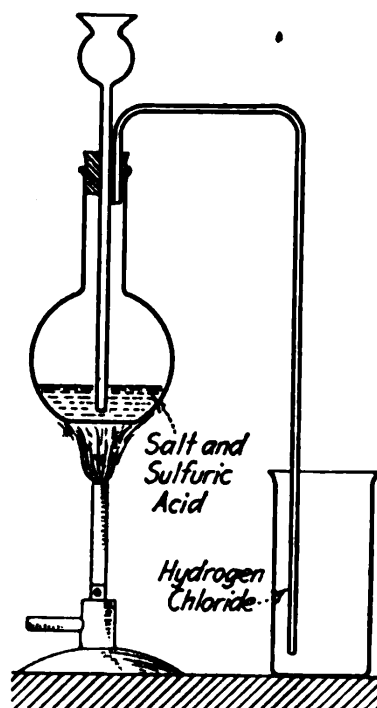


FIG. 21.

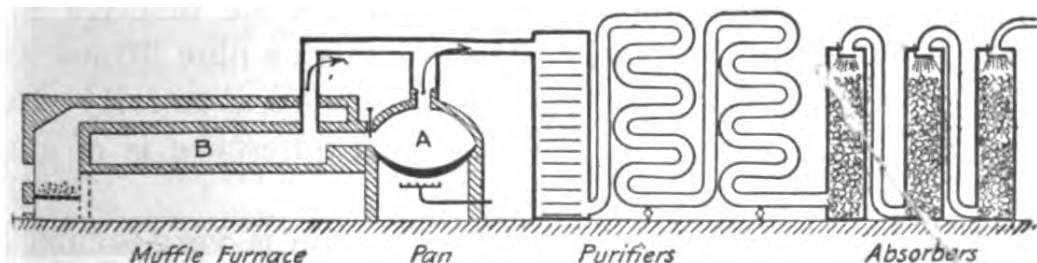


FIG. 22.

The reactions just given are reversible and would be incomplete were it not for the fact that the hydrogen chloride is very volatile and hence readily distilled from the mixture. This, of course, decreases the concentration of the hydrogen chloride, and more is at once formed to take its place. This will continue until the

salt and sulfuric acid have been completely transformed, provided that the hydrogen chloride is carried off as it is formed.

The action takes place not because the hydrochloric acid is a weaker acid than sulfuric acid—it is much stronger—but because the hydrochloric acid is much more volatile than sulfuric acid. In fact sulfuric acid may be replaced by any acid, however weak, which is much less volatile than hydrochloric acid and which is not a strong enough oxidizing agent to attack the latter. Phosphoric acid will do very well.

**First General Method for the Preparation of Acids.**—In the cases given above we are dealing with examples of a general method for the preparation of acids from their salts. This may be called the first general method for the preparation of acids and may be stated as follows. *Treat a salt of the acid desired with a less volatile acid and distil. It is applicable to such acids as will stand distillation without decomposition, and of course the added acid must not only be less volatile than the acid desired but must also be without action upon this acid.*

**Properties of Hydrogen Chloride.**—A number of properties of hydrogen chloride have already been given; in addition we may state that its density is 0.00164 and molecular weight, 36.47. Its critical temperature is  $51.4^{\circ}\text{C}$ . and its critical pressure 81.6 atmospheres. It can then be converted into a liquid by pressure alone at ordinary temperatures. At  $22^{\circ}\text{C}$ . the pressure necessary is 46 atmospheres. The boiling-point of the liquid hydrogen chloride is  $-83^{\circ}\text{C}$ . and the freezing-point is  $-110^{\circ}\text{C}$ . The liquid hydrogen chloride is a colorless almost inactive substance which is without action upon metals or blue litmus, and in general exhibits very little of the great chemical activity which is shown by its solution in water. This difference is of great import as we shall soon see.

As has been mentioned, hydrogen chloride is very soluble in water. At its freezing-point one volume of water will absorb about 525 volumes of hydrogen chloride. At the same time a great amount of heat is developed which points to the formation of a compound with the water. This is indicated too by the fact that hydrogen chloride does not follow Henry's law of solubility of gases which states that *provided no chemical reaction takes place between the gas and the solvent, the mass of the gas dis-*

solved by a given mass of the solvent is directly proportional to the pressure. In the case of hydrogen chloride and water, Henry's law is far from describing the behavior. In fact the mass of the hydrogen chloride dissolved is but slightly altered by large changes in pressure. This would indicate that the hydrogen chloride undergoes some sort of a change upon passing into solution in water. As a matter of fact, by cooling very concentrated solutions of hydrogen chloride to low temperatures, three crystalline compounds of hydrogen chloride and water can be obtained. These are the mono-, di- and tri-hydrates, and have the formulas  $\text{HCl}\cdot\text{H}_2\text{O}$ ,  $\text{HCl}\cdot 2\text{H}_2\text{O}$ , and  $\text{HCl}\cdot 3\text{H}_2\text{O}$ .

**Constant Boiling Hydrochloric Acid.**—Hydrogen chloride boils at  $-83^\circ\text{C}$ . and water at  $100^\circ\text{C}$ . so one would naturally

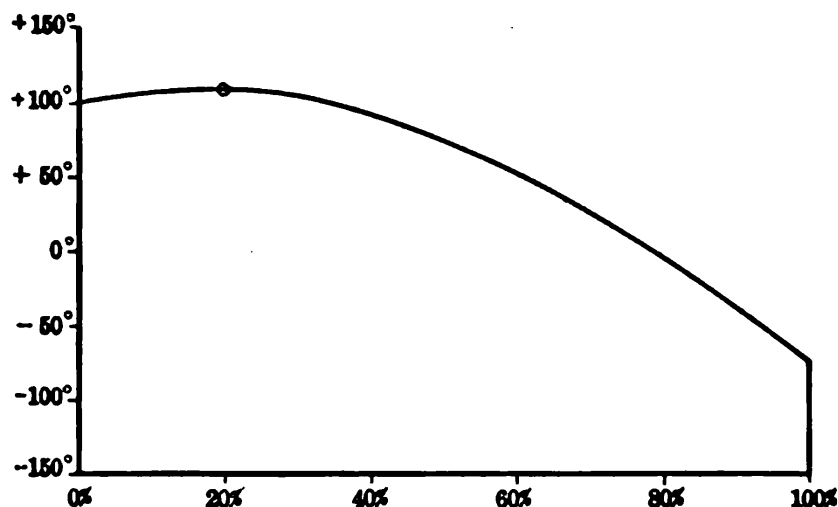


FIG. 23.

expect that a solution of hydrogen chloride would boil at temperatures between these two points. This is true, however, only of solutions containing more than 40 per cent. of hydrogen chloride. Weaker solutions boil at temperatures above  $100^\circ\text{C}$ . and a 20 per cent. solution boils at  $110^\circ\text{C}$ . and is the highest boiling and consequently the least volatile mixture of hydrogen chloride and water. If one distils a hydrochloric acid solution of less than 20 per cent. both water and hydrogen chloride come off, but relatively more of the former, and the residue becomes richer and richer in hydrogen chloride. After this process has gone on for some time, the residue finally reaches 20 per cent. hydrogen chloride which is the least volatile of the hydrogen chloride-

water mixtures, and boils at  $110^{\circ}\text{C}$ . After this has been reached, the mixture distils unchanged in composition and boiling-point.

If on the other hand we start to distil a hydrochloric acid solution containing more than 20 per cent. hydrogen chloride, this substance will come off with the water but in such quantities that the distillate contains a higher percentage of hydrogen chloride than the original mixture, leaving a residue which contains a smaller percentage of hydrogen chloride and boils at a higher and higher temperature until its boiling-point becomes  $110^{\circ}\text{C}$ . and its composition 20 per cent. hydrogen chloride. After this it boils constantly with unchanged composition. From the above it follows that no matter what the original composition of the hydrochloric acid, after it has boiled for sufficient time the residue will be a 20 per cent. acid boiling at  $110^{\circ}\text{C}$ .

The relationship between the composition and boiling-point for hydrochloric acid is shown in Fig. 23.

This constant boiling hydrochloric acid has often been mistaken for a chemical compound, but that this is not the case is shown by the fact that its composition changes with the pressure. When the boiling is carried out under a pressure of 2.5 atmospheres, the composition is 18 per cent. hydrogen chloride, while at 0.066 atmospheres it is 23 per cent. hydrogen chloride.

## CHAPTER IX

### IONIC THEORY

The Ionic Theory, or the Theory of Electrolytic Dissociation as it is often called, is one of the most important tools of modern chemistry, and this chapter will be devoted to its development. As should always be the case, the facts which it was devised to explain will be given first and should be fully appreciated by the student, and then the theory learned not as a fact, but as a possible explanation for the facts.

**Acids.**—Mention has been frequently made in what has gone before of acids; hydrochloric, sulfuric and phosphoric acids are typical examples of this very important class of compounds. The acids comprise a large group of substances of very different compositions which have certain well marked properties in common. For example, they all contain hydrogen as one of their essential constituents, and when in solution they all taste sour, redden litmus, and evolve hydrogen gas when brought in contact with magnesium or zinc. All acids are hydrogen compounds, but many hydrogen compounds are not acids. Water, turpentine, sugar, olive oil, and many other substances contain hydrogen but will not evolve hydrogen when brought in contact with magnesium or zinc at ordinary temperatures, neither do they taste sour, nor redden litmus, and so are not acids. The hydrogen, then, of acids must be in some kind of a special condition, different from that of the hydrogen of other compounds, and since this is the only constituent which acids have in common, as is shown by the appended list of acids and their formulas, the common properties of acids must be ascribed to the hydrogen in this special condition.

#### SHORT LIST OF THE MORE COMMON ACIDS

Hydrochloric acid,	HCl	Nitric acid,	HNO <sub>3</sub>
Hydrobromic acid,	HBr	Phosphoric acid,	H <sub>3</sub> PO <sub>4</sub>
Hydriodic acid,	HI	Oxalic acid,	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>
Sulfuric acid,	H <sub>2</sub> SO <sub>4</sub>	Acetic acid,	HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>

The acids show their peculiar properties only when dissolved in water and a few other solvents. When in a perfectly pure state or dissolved in most solvents, they are as indifferent as pure hydrogen chloride and neither redden litmus nor evolve hydrogen with magnesium. Of course, their taste in the entire absence of water cannot be determined. The water has then something to do with the transformation of the hydrogen of the acids into its special state. In this connection it will be recalled that there is evidence that hydrogen chloride undergoes a chemical change when it passes into solution in water.

**Bases.**—Bases are another rather large class of substances of varied composition which like acids, have, when dissolved in water, certain properties in common. Their solutions all have a peculiar alkaline taste, a soapy feeling, and turn red litmus blue. As will be seen from the partial list of bases given below, they all contain hydrogen and oxygen in the proportion of one atomic weight of the one to an atomic weight of the other. We express this by saying that they contain the hydroxyl group, OH, and ascribe their common properties to this group.

#### LIST OF BASES

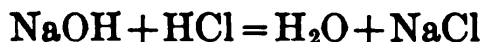
Sodium hydroxide,	NaOH	Calcium hydroxide,	Ca(OH) <sub>2</sub>
Potassium hydroxide,	KOH	Barium hydroxide,	Ba(OH) <sub>2</sub>
Ammonium hydroxide,	NH <sub>4</sub> OH	Strontium hydroxide,	Sr(OH) <sub>2</sub>

Like the acids, these bases show their common properties only when dissolved in water and a few other solvents, and since there are many compounds known which contain hydroxyl and yet are not bases, we ascribe the characteristic properties of bases in water solution to the hydroxyl in a peculiar condition, similar to that of the hydrogen from acids in such solutions.

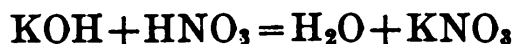
**Neutralization.**—When a solution of hydrochloric acid is added to a solution of sodium hydroxide in just the proper proportions, both the characteristic properties of the acid and those of the base completely disappear, and the solution which is left behind neither turns blue litmus red nor red litmus blue. It has neither a sour nor an alkaline taste, has no soapy feeling and does not evolve hydrogen at ordinary temperatures with zinc or magnesium. Its taste is a pure salty one and in fact it is in every way identical with a solution of common salt, sodium chloride,

in water. If the solution be evaporated, nothing but water passes off, and nothing but sodium chloride is left behind. What then has become of the hydroxyl of the base and the hydrogen of the acid? Obviously they must have combined to form water, leaving the sodium and chlorine to form sodium chloride.

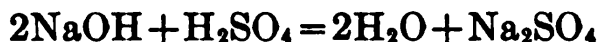
The reaction may be represented by the equation



We say that the hydrochloric acid and sodium hydroxide have neutralized each other and that water and a solution of sodium chloride have been formed. Other acids and bases behave in much the same way. They neutralize each other and leave solutions of the corresponding salts. For example, potassium hydroxide and nitric acid give water and a neutral solution of potassium nitrate,  $\text{KNO}_3$



Sulfuric acid gives sulfates and water



**Reacting Ratio in Neutralization.**—By inspection of the above equations and writing others, it is very easy to satisfy one's self that a quantity of a base which contains 17.008 gm. of hydroxyl will just neutralize a quantity of an acid which contains 1.008 gm. of hydrogen in the peculiar acid condition. Since it is a very easy matter to tell with the aid of litmus just when a solution is neutral, the fact mentioned above is made the basis of a simple and much used method for the quantitative determination of acids and bases. The essentials of the method are as follows: Such a quantity of a base, say sodium hydroxide, as will contain 17.008 gm. of hydroxyl is dissolved in water and the solution made up to just a liter. Each cubic centimeter will then contain 0.017008 gm. of hydroxyl and will neutralize that quantity of an acid which will contain 0.001008 gm. of hydrogen, that is to say, 0.03647 gm. of hydrogen chloride for example. Such a solution is called a **normal solution** of a base. To use this in determining the amount of an acid, say hydrogen chloride, in a solution of unknown strength one would weigh

out a few grams of the acid, add a drop of litmus solution and then run in from a graduated vessel called a burette (Fig. 24), enough of the normal hydroxide solution so that the litmus is just on the point of turning blue, and in fact is neither blue nor red. The number of cubic centimeters used multiplied by 0.03647 gives the weight of hydrogen chloride in the acid solution

taken. Suppose that we weighed out 10 gm. of the acid and it required 20 c.c. of the normal base to neutralize it. The acid contained in this 10 gm. is

$$20 \times 0.03647 = 0.7294 \text{ or } 7.294 \text{ per cent.}$$

Similarly with the aid of a normal acid, i.e., one containing 1.008 gm. of hydrogen in the acid condition per liter, one may determine very easily the quantity of base in a solution of unknown strength.

Methods like the above are in very frequent use in quantitative chemical analysis, and are called volumetric methods.

**Acids, Bases, and Salts have two Sets of Properties.**—Every acid has when in solution in water, two independent sets of properties, one common to all acids and evidently belonging to the hydrogen

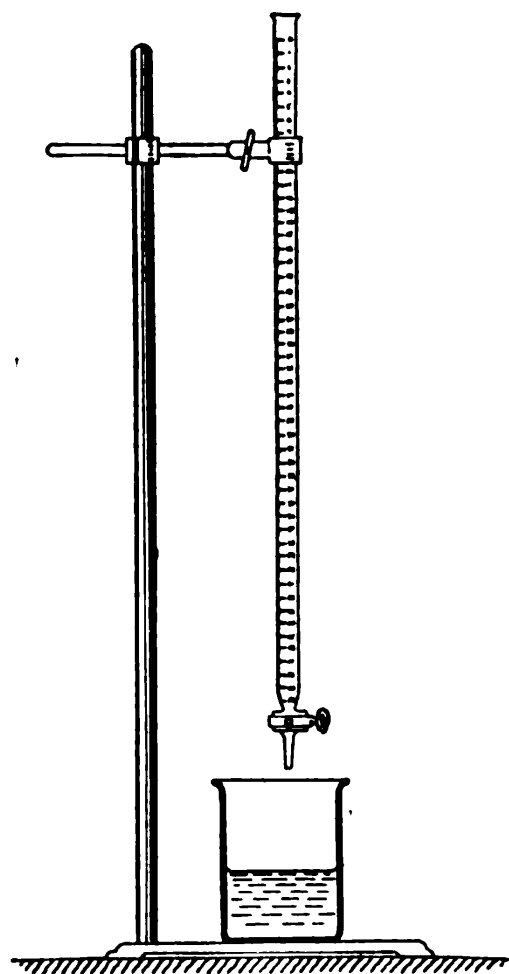


FIG. 24.

of the acid, and the other peculiar to that acid, being shown by no other acid, and evidently belonging to the rest of the acid other than the hydrogen. For example, hydrochloric acid is like all other acids in that it is sour, reddens litmus and gives hydrogen with zinc, but differs from all other acids in that it will give sodium chloride with sodium hydroxide, and also will yield a white curdy precipitate with silver nitrate which precipitate is silver chloride. A few other acids give somewhat similar precipitates with silver salts, but these all differ sufficiently

in their properties from the silver chloride so that they may be positively distinguished from the latter.

Bases too have two independent sets of properties in water solutions, the one common to all bases and evidently due to the hydroxyl, and the other peculiar to the particular base that is being worked with and belonging to the rest of the base other than the hydroxyl. For example, barium hydroxide shows all the characteristic properties of bases, turning litmus blue, etc., and also gives with sulfuric acid and all sulfates a white precipitate of barium sulfate,  $\text{BaSO}_4$ , which is different in its properties from all other substances. No other base has just this property. When one of these acids with its two sets of properties is neutralized by a base with its two sets, the properties common to all acids together with those common to all bases completely disappear leaving behind that set of properties of the acid which was peculiar to that particular acid, and the set of properties of the base which was peculiar to that base. So the salt solution remaining after the neutralization of an acid by a base has two sets of properties.

It follows from what has just been said that solutions of hydrochloric acid and all soluble salts of hydrochloric acid should give the white curdy precipitate of silver chloride upon the addition of silver nitrate. This is exactly what has been found to be the case. Similarly barium salts formed by the neutralization of this base by acids should and do give precipitates of barium sulfate upon the addition of sulfuric acid or sulfates.

When these same bases, acids and salts are in the pure state or even in solution in most solvents other than water, they do not exhibit these two sets of independent properties, but each has only one. An explanation for these and for the succeeding sets of facts will soon be given as the theory of electrolytic dissociation.

**Abnormal Lowering of the Freezing-point.**—In connection with the discussion of hydrogen peroxide it was brought out that a gram mole of a normal substance lowers the freezing-point of 1,000 grm. of water  $1.85^\circ\text{C}$ . and that this may be made the basis of a method for the determination of molecular weight. In fact we got the molecular weight of hydrogen peroxide in this way. The law of the molecular lowering of the freezing point is more exact for dilute solutions than for concentrated ones and we will

be more accurate if we state it as follows: A gram mole of a normal substance lowers the freezing point of 1000 kgrm. of water  $0.00185^{\circ}\text{C}$ .

The acids, bases and salts are the exceptional substances which do not lower the freezing-point of 1,000 kgrm. of water  $0.00185^{\circ}\text{C}$ . per gram mole, but always produce a greater lowering. In many cases the lowering is nearly twice what we would expect, in others something like three times, and sometimes even more than three times the  $0.00185^{\circ}\text{C}$ . per gram mole dissolved in 1,000 kgrm. of water.

For example, hydrogen chloride is a gaseous substance and its molecular weight can be found from its gaseous density to be 36.47. If one dissolves 36.47 gm. of hydrogen chloride in 1,000 kgrm. of water, the freezing-point of the water is lowered almost twice  $0.00185^{\circ}\text{C}$ . A gram mole of sodium or potassium chloride or of any other salt formed by the union of one atomic weight of a metal with one atomic weight of chlorine produces about the same lowering as a gram mole of hydrogen chloride when dissolved in 1,000 kgrm. of water or about twice  $0.00185^{\circ}$ . Such salts as calcium or barium chloride,  $\text{CaCl}_2$  or  $\text{BaCl}_2$ , which contain two atomic weights of chlorine to one atomic weight of the metal, lower the freezing-point nearly three times  $0.00185^{\circ}$  per mole of salt in 1,000 kgrm. of water. From these facts it looks as though the lowering for salts were  $0.00185^{\circ}\text{C}$ . per gram atomic weight of each element instead of per gram mole. That this is not the case is shown by the fact that nitric acid,  $\text{HNO}_3$ , potassium nitrate,  $\text{KNO}_3$ , and sodium nitrate,  $\text{NaNO}_3$ , only lower the freezing-point of 1,000 kgrm. of water approximately twice  $0.00185^{\circ}$  per gram mole of acid or salt. In more concentrated solutions these acids and salts give lowerings which are abnormal but not as much so as in the dilute solutions; however, even in the most dilute solutions the abnormality is never greater than the figures just given. These facts are very significant and important in connection with the theory soon to be developed.

**Electrolytes.**—Metals are called conductors of the first class. As is well known, they are not altered in any way by the current except that their temperature is more or less raised. Some solutions are also conductors of electricity and are called conductors of the second class because they are not only become

heated, but also are invariably decomposed during the passage of the current provided the circuit consists in part of conductors of the first class as is usually the case. Such solutions are called electrolytes and are formed only when acids, bases, and salts are dissolved in water or in the few other solvents in which they each show their two independent sets of properties. The decomposition takes place at points where the electric current enters and leaves the salt solution. The terminals of the metallic portion of the circuit are called electrodes and are distinguished from each other by calling that electrode where the electricity

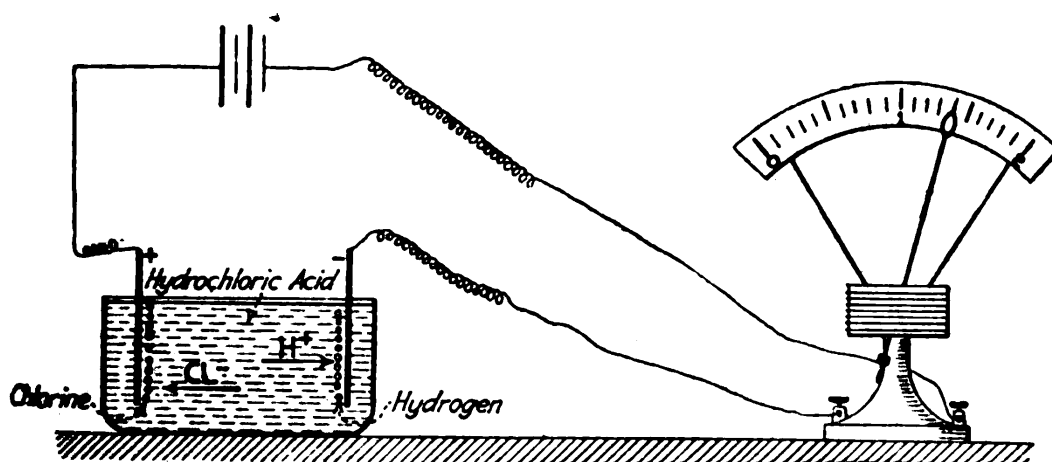


FIG. 25.

enters the solution the anode and that where it leaves it for the metal, the cathode. During the passage of the current, one kind of substance appears at the cathode and an entirely different substance at the anode. When hydrogen chloride solution is electrolyzed Fig. 25, hydrogen appears at the cathode and chlorine at the anode. The two substances appearing at the electrodes are in general the two substances which seem to give to the salt solutions their two sets of independent properties.

A fact which is closely connected with those given above, and which is still more significant is that, when a current of electricity is passed through a salt solution, the two components of the salt which act chemically independently of one another may actually be seen to move slowly in opposite directions, the one toward the cathode and the other toward the anode, and at quite different rates. Especial precautions must be taken to bring this out, but the experiments are rather easily performed and are quite definite in their results.

In the case of hydrochloric acid solutions, the chlorine moves toward the anode while the hydrogen travels toward the cathode, and moves nearly five times as rapidly as the chlorine.

**The Law of Faraday.**—The English scientist Faraday in the year 1833 carefully investigated the phenomena occurring at the electrodes and devised the names which we have been using such as electrolysis, electrolyte, electrode, anode, cathode, and in addition he called the substances which travel toward the electrodes ions. Those which move toward the cathode being the cations and those which move toward the anode being the anions. He also discovered facts which are described by the following law known as the Law of Faraday.

*Electricity moves in electrolytes only with the simultaneous movement of their chemically independent components, and is accompanied by the deposition of two different substances upon the electrodes, the quantity of electricity required to liberate a gram atomic weight of any substance being 96,500 coulombs or some integral multiple of this.*

**Summary.**—We have now discussed the principal groups of facts which the theory of electrolytic dissociation was devised to explain, but before proceeding to the theory itself a brief summary of these facts may be of use.

**First.**—Salts in solution in water show two independent sets of chemical properties; all salts having a common component have one set of properties in common. The term salt as used here includes acids and bases as well as salts in the ordinary sense.

**Second.**—Salts in solution in water lower the freezing-point of the water more than  $0.00185^{\circ}\text{C}$ . per gram mole per 1,000 kgm. of water; some nearly twice, some three times, and some even more than three times the normal lowering.

**Third.**—Salts in solution are electrolytes and the electricity passes through the solution only with the simultaneous movement of the components of the salts in opposite directions and at quite different rates. In addition two different substances are liberated at the electrodes. One gram atomic weight of each substance is liberated by the passage of 96,500 coulombs or some rational multiple of this.

All these are well established facts. The theory which is about to be given is simply an imagined cause or explanation for these

facts and is in many respects on a par with the atomic theory. It is very useful in correlating a great many facts of chemistry and has been very successful in predicting the discovery of new facts, and hence is worthy of considerable attention.

**The Theory of Electrolytic Dissociation.**—To explain the facts outlined above, certain **assumptions** are made concerning the nature of salts in solution. The first one is that when salts are dissolved in water, they are immediately decomposed or dissociated into at least two different substances which are chemically separate and distinct from each other and from the original salt. These new substances are assumed to be the chemically independently acting components of the salts and are called **ions**, from the Greek word *ἰών* meaning wander, because they move in opposite directions toward the electrodes. That which goes toward the anode is known as the **anion** and that toward the cathode as the **cation**.

Each gram mole of salt which dissociates is assumed to give rise to at least 2 gram moles of these new substances, the ions, and each gram mole of an ion, or for brevity "gram ion," is assumed to act in lowering the freezing-point of water like a gram mole of any other substance.

To account for the electrical properties of salt solutions, it is assumed that these new substances, the ions, are charged with electricity, the cations with positive and the anions with negative electricity; the charges amounting to 96,500 coulombs or a integral multiple per gram ion. Since salt solutions are electrically neutral, it must be assumed that the + charges upon the cations just equal the - charges upon the anions.

The **explanation** of the first group of facts, p. 108, by the theory is very simple. We have only to say that each of the two independent sets of properties belongs to one of the new substances or ions formed by the dissociation of the salt, and since these ions are assumed to be uncombined, each set of properties is of course independent of the other component of the salt. The chlorine ion is assumed to be identical whether it comes from hydrochloric acid, HCl, sodium chloride, NaCl, potassium chloride, KCl, or any other chloride, and hence all chlorides in solution show the properties of chlorine as ion no matter what the other ion may be. The acid properties are ascribed to hydrogen as ion and since this

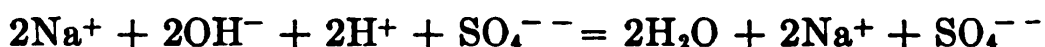
In terms of this theory a **salt** is any substance which when dissolved in water yields ions.

An **acid** is a salt which when dissolved in water gives hydrogen as one of its ions.

A **base** is a salt which when dissolved in water gives hydroxyl as one of its ions.

**Neutralization of Acids and Bases.**—When we come to consider the neutralization of acids and bases in the light of the theory, we reach the rather surprising conclusion that in the process only water is formed. The salt in the narrow sense, is not formed since its cation and anion existed as such in the solution of the base and acid before they were brought together and continue to do so after the process is finished.

To illustrate, let us give the equations for a few reactions of this kind.



In every case water is formed and water only. The cation of the base and the anion of the acid are left unaltered. This explains why these salt solutions show the properties which were peculiar to the particular base and acid from which they were formed.

**Heat of Neutralization.**—Whenever any of the acids and bases given in the above list neutralize each other there is always 57 Kj. of heat evolved per mole of water produced, and this is true of all other strong acids and bases as well. This fact is very easy to explain on the basis of the electrolytic dissociation theory. In the light of this theory, water is the sole product of these reactions and is always formed from the same substances, hydrogen as ion and hydroxyl as ion, and therefore each reaction should show the same heat effect; and thus 57 Kj. or 13,600 cal. is the heat of formation of water from hydrogen and hydroxyl as ions. If

the salts had really been formed, the heat effect should have been different in each case.

**Action of Acids.**—In our previous discussion of acids, certain points of similarity, their taste, action on litmus, metals, etc., were made much of and ascribed to their common constituent hydrogen, in what we termed the ionic state. In other respects acids show great similarity. Quantities of different acids which contain equal amounts of ionizable hydrogen are equivalent to each other in several ways. They will, for example, neutralize the same quantity of any given base, say sodium hydroxide, and also when brought in contact with an excess of metal, like zinc, evolve equal quantities of hydrogen. Such quantities of acid as contain equal weights of ionizable hydrogen are appropriately called equivalent quantities, and that weight of any given acid which contains 1.008 grm. of ionizable hydrogen is called a gram equivalent of that acid. It will be recalled that a gram equivalent of an acid in 1,000 c.c. of solution is called a normal solution of the acid.

In some respects acids show striking points of dissimilarity. If pieces of zinc of equal area are introduced into equivalent solutions of hydrochloric, sulfuric, and acetic acids, hydrogen will be evolved in each case, but at very different rates in the different acids. If normal acids are used, less than 1 c.c. of hydrogen will be liberated from the acetic acid, and 65 c.c. from the sulfuric acid during the time required for the liberation of 100 c.c. from the hydrochloric acid. If equivalent quantities of the acids and an excess of zinc are used, ultimately, equal quantities of hydrogen will be liberated from each. In order to insure the success of the experiment indicated above, the pieces of zinc, before use should be treated with a dilute solution of copper sulfate. Copper will be deposited on the zinc and will tend to overcome the disturbing influence of local impurities in the zinc and secure a uniform evolution of hydrogen.

If we examine other cases in which these acids take part in reactions at measurable rates, we discover that their rates stand in the same order as in their action on zinc.

Much the same relationship exists between the lowering of the freezing-points of these acids. One gram mole of hydrochloric acid, it will be recalled, lowers the freezing-point of 1,000 grm.

of water nearly twice the normal lowering of  $1.85^{\circ}$  per gram mole; while a gram mole of acetic acid per 1,000 grm. of water lowers it only a trifle more than  $1.85^{\circ}$ .

Normal solutions of these acids show very much these same differences in their power to conduct electricity. The solution of hydrochloric acid is a good conductor; sulfuric acid something like two-thirds as good; while acetic acid, although still a conductor, is a poor one.

Because of these peculiarities in their actions, everyone calls hydrochloric and sulfuric acids strong acids, and acetic acid a weak acid. The hydrochloric acid is considered to be somewhat stronger than sulfuric.

**Explanation.**—It is a very simple matter to explain the facts outlined above with the aid of the ionic theory. We have only to add to our previous assumptions, that all acids break up or ionize so as to give hydrogen as ion, and that this hydrogen as ion has the characteristic acid properties, the further assumption that the various acids differ among themselves in the extent to which they break up, or in their degree of ionization. Hydrochloric acid is assumed to break up or ionize so far that in normal solution the greater part of the substance has been changed into hydrogen and chlorine as ions, while under the same conditions only a very small part of the acetic acid is supposed to be ionized; while sulfuric acid stands between the other two. Naturally, if hydrogen as ion is the hydrogen which acts acid, that solution which contains the greatest concentration of hydrogen present actually as ion will be the most intensely acid. This, from what has been said, would be the hydrochloric acid, then would come sulfuric and last the acetic far behind the other two.

We have learned that the rate at which any given substance will react, other things being equal, depends upon the concentration, and further that in terms of the ionic theory the reaction between an acid and zinc is between hydrogen as ion and the zinc. From all that has been said above, then, it follows that the rate of evolution of hydrogen gas from these three acids should stand in the order, hydrochloric, sulfuric, and acetic acids. This was the order found by experiment.

But if the acids differ so much in their degree of dissociation or ionization, how does it happen that equivalent quantities will

neutralize the same amount of sodium hydroxide or any other base, and also ultimately evolve the same quantity of hydrogen when acted upon by an excess of a metal? To explain this we have only to assume that the ionization of an acid is a reversible process, and that as the hydrogen as ion is used up by combining with hydroxyl or reacting with the metal, more of the undissociated acid will break up into ions, and that this process will continue until the undissociated acid is completely used up.

The total acid hydrogen of an acid is called the ionizable hydrogen and that fraction of it which is present at any one instant in the state of the free ion, is called the actual ion, while that which is undissociated, but capable of becoming ionized, is called the potential ion. The ionizable hydrogen is the sum of the actual and the potential ions. Equivalent quantities of these three acids then contain the same amount of ionizable hydrogen, but differ in the relative proportions of the actual and potential ions; hydrogen chloride having the most actual and acetic the least.

The explanation of the difference in the lowering of the freezing-point is so obvious that it need not be gone into here.

The ability of a gram mole of an electrolyte to conduct electricity is called its molecular conductivity. It may be determined by ascertaining the number of amperes of electricity which will flow through a conductivity cell when the whole of the solution containing a gram mole of the solute is placed between electrodes 1 cm. apart and a potential of 1 volt is applied.

As a rule the molecular conductivity of a salt increases as the volume of the solution in which one gram mole is dissolved is increased, *i.e.*, as the solution is diluted. With the great majority of electrolytes, the molecular conductivity increases with the dilution up to a certain point, and then runs along without any material increase as far as the measurements can be carried—in other words, it reaches a maximum.

A natural explanation for this is that the molecular conductivity of a solution is proportional to the fraction of the gram mole which is present as ions or the degree of ionization or dissociation as it is called and to the speed with which the ions move.

Assuming that the latter is constant as the solution is diluted, it follows that the degree of ionization of the electrolyte increases with the dilution, and that when the conductivity has reached its maximum, the salt is entirely ionized or completely dissociated. The degree of dissociation at any given dilution, can be found by dividing the molecular conductivity at that dilution by the maximum molecular conductivity at very great dilution. The results given in the following table have been obtained in this way. Dilution as used here means the number of liters of the solution which contains one gram mole of the acid. It will be seen from this table that even at moderate dilutions, the first three acids are almost completely dissociated and are about as strong as possible. The sulfuric acid is distinctly weaker, but quickly gains in strength. The hydrofluoric and acetic acids are much weaker, but grow rapidly stronger. So the more dilute the acids the stronger they become in the sense that they are more largely dissociated. *That acid is the strongest which is most easily broken up into its ions.* No adequate reason has been offered as to why hydrochloric acid is so highly and acetic acid so slightly dissociated.

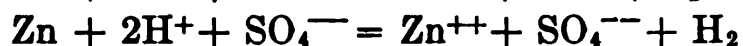
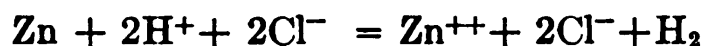
Dilution	HCl	HBr	HI	HF	H <sub>2</sub> SO <sub>4</sub> <sup>1</sup>	HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>
1	0.784	.....	.....	0.07	0.51	0.004
10	0.95	0.95	0.95	0.10	0.57	0.013
100	0.98	0.98	0.98	0.26	0.79	0.050
1,000	0.99	0.99	0.99	0.95	0.93	0.125

Bases, like acids, differ widely in the degree of their dissociation at moderate dilutions. Sodium and potassium hydroxides being highly dissociated. Calcium and barium hydroxides have about the same degree of dissociation as sulfuric acid at any given dilution, while ammonium hydroxide is weak like acetic acid.

Salts, in the common sense of the term, are with few exceptions highly dissociated, and that too whether they are salts of weak or of strong acids. Sodium acetate, for example, at any given dilution is only a little less dissociated than sodium chloride.

<sup>1</sup> The sulfuric acid solutions are equivalent and not molecular solutions.

**Hydrogen Ion as An Oxidizing Agent.**—When an acid acts upon a metal and hydrogen is given off, the reaction seems to be between the hydrogen ion and the metal. For example, the equations



indicate that neither the chlorine nor the sulfate ion is changed, while the zinc is transformed from the metal to the ion and the hydrogen from the ion to the free element. This change of the zinc from the metal to the ion is considered oxidation and the hydrogen ion is the oxidizing agent. This type of oxidation must be kept in mind until a full definition of oxidation and reduction can be offered.

## CHAPTER X

### OXYGEN COMPOUNDS OF CHLORINE

**General.**—Neither oxygen and chlorine nor oxygen, hydrogen and chlorine combine directly, but by more or less roundabout methods three oxides and four acids containing oxygen, oxyacids as they are called, can be prepared. The following table gives the names and formulas of the acids, the sodium salts of these acids, and the oxides.

ACIDS		SALTS	
HCl.....	Hydrochloric acid	NaCl.....	Sodium chloride
HClO.....	Hypochlorous acid	NaClO.....	Sodium hypochlorite
HClO <sub>2</sub> .....	Chlorous acid	NaClO <sub>2</sub> .....	Sodium chlorite
HClO <sub>3</sub> .....	Chloric acid	NaClO <sub>3</sub> .....	Sodium chlorate
HClO <sub>4</sub> .....	Perchloric acid	NaClO <sub>4</sub> .....	Sodium perchlorate

#### OXIDES

Cl<sub>2</sub>O, Chlorine monoxide or hypochlorous anhydride.  
ClO<sub>2</sub>, Chlorine dioxide or chlorine peroxide.  
Cl<sub>2</sub>O<sub>7</sub>, Chlorine heptoxide or perchloric anhydride.

These oxyacids and their salts furnish excellent illustrations of the law of multiple proportions.

**Nomenclature of Acids and Salts.**—The names of acids formed by the union of hydrogen with one other element and which consequently do not contain oxygen are formed by taking the characteristic part of the name of the element other than hydrogen and adding the prefix hydro- and the suffix -ic. For example hydro-chlor-ic acid. Salts of such acids are named by combining the name of the metal which replaces the hydrogen of the acid with another word formed by dropping the prefix hydro- from the name of the acid and replacing the -ic by -ide. For example, sodium chloride.

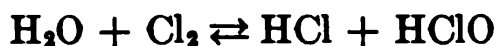
In naming the oxyacids the best known is usually designated by adding to the characteristic part of the name of the element

other than hydrogen and oxygen the suffix -ic. For example,  $\text{HClO}_3$  is called chloric acid. The names of the salts of such acids end in -ate, as sodium chlorate,  $\text{NaClO}_3$ .

If there is an acid containing more oxygen than the -ic acid, it is distinguished by adding to the name of the -ic acid the prefix per- and similarly for the salt as perchloric acid,  $\text{HClO}_4$ , and sodium perchlorate. That acid containing the next smaller amount of oxygen than the -ic acid is distinguished by the suffix -ous and its salts are called the -ites. For example, chlorous acid,  $\text{HClO}_2$ , and sodium chlorite.

If there is an acid containing a still smaller amount of oxygen than the -ous acid, it is distinguished by adding to the name of the -ous acid the prefix hypo- and its salts are called hypo- . . . -ites; for example, hypochlorous acid and sodium hypochlorite.

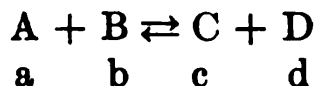
**The Preparation of the Oxygen Compounds of Chlorine.**—The first step in the preparation of the oxygen compounds of chlorine is the reaction between water and chlorine.



From the hypochlorous acid so formed, hypochlorites can be prepared by neutralization with bases. From these hypochlorites by appropriate means chlorates, perchlorates, chlorites, and the oxides of chlorine may be made. The reaction between chlorine and water is therefore an important one and may appropriately be called the key reaction for the oxygen compounds of chlorine. It is reversible and is very incomplete under ordinary circumstances. Equilibrium results in this and other reversible reactions when the conditions described in what is known as the Law of Mass Action are fulfilled. In order that we may have a proper mastery of these reversible reactions, this law will now be developed.

**The Law of Mass Action.**—The law of mass action in the form in which it is to be developed here, applies to reversible reactions in equilibrium at constant temperature. Let us take a general case and say that we have a reversible reaction between A and B for the formation of C and D. Let a, b, c, and d represent the concentrations of A, B, C, and D respectively, and let R stand for the rate at which A and B combine for the formation of C and D,

and  $R'$  for that at which C and D react for the re-formation of A and B,



Then from what we have already learned, p. 44, the rate at which A and B react, everything else being constant, is proportional to  $a$ , and likewise to  $b$ , and therefore is proportional to their product since a number proportional to each of two or more numbers is proportional to their product or

$$R = Ka$$

$$R = K'b$$

$$R = K''ab$$

Correspondingly  $R'$  the rate at which C and D react is proportional to the concentration of C and to that of D and hence to the product of these concentrations

$$R' = K'''c$$

$$R' = K''''d$$

$$R' = K'''''cd$$

Equilibrium will result in all such reactions when the two rates are equal, and therefore at equilibrium

$$R = R'$$

Hence

$$K''ab = K'''''cd$$

or

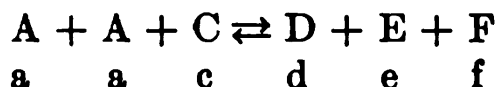
$$\frac{K''}{K'''''} = \frac{cd}{ab} = k$$

Expressed in words this would be: The product of the concentration of the resulting substances divided by the product of the concentration of the reacting substances is a constant for a reversible reaction in equilibrium at constant temperature. From this it follows that if the three substances A, B, and C react to form D, E, and F, equilibrium will result when  $def/abc$  reaches a certain definite constant value whose magnitude depends upon the nature of the substances and the temperature, but not upon the particular values of the concentrations which happen to exist

in any one case. What is called the mass law equation for this reaction is:

$$\frac{def}{abc} = K$$

Suppose now that A is identical with B, then "a" will be identical with "b." The chemical equation then becomes



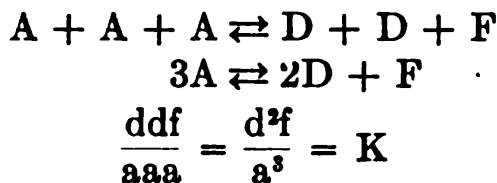
or



and the mass law equation,

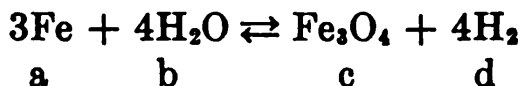
$$\frac{def}{aac} = \frac{def}{a^2c} = K$$

If A is identical with B and C and if D and E are identical, these equations become,



This may be expressed in words as follows: *When equilibrium results in a reversible reaction at constant temperature, the product of the concentration of the resulting substances divided by the product of the concentrations of the reacting substances—each concentration raised to that power whose exponent is the coefficient of the substance in the chemical equation—is a constant.* The content of this statement is the *Law of Mass Action*.

For an example of its application we may take the equilibrium between water vapor, iron, iron oxide, and hydrogen. The equation is



The mass law equation is

$$\frac{cd^4}{a^3b^4} = K$$

Since solids and liquids change their volume so slightly with changes of pressure, it follows that the ratio of their mass to their

volume is practically constant; therefore the concentration of a solid substance or of a homogeneous liquid is constant and only gases and dissolved substances have variable concentrations.

The iron and the iron oxide are solids so their concentrations are constant and may be combined with the equilibrium constant  $K$ . The conditions of equilibrium are therefore dependent upon the concentrations of the hydrogen and of the water vapor. The mass law equation then becomes

$$\frac{d^4}{b^4} = \frac{Ka^3}{c} = k$$

or

$$\frac{d}{b} = \sqrt[4]{k}$$

This then tells us that these substances will be in equilibrium when there is a certain definite ratio between the concentrations of the hydrogen and of the water vapor.

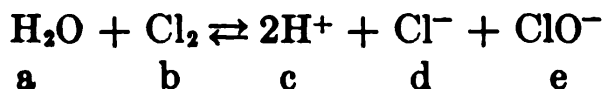
It is very easy to see from this that if the concentration of the hydrogen be decreased, the water must react with the iron for the formation of more hydrogen and iron oxide. In a current of steam which sweeps away the hydrogen, equilibrium will never be reached and the reaction will continue until all the iron is used up.

The law of mass action is exceedingly useful in that it enables one to tell just what to do to make a reversible reaction run in either direction as desired, and further, if we know the magnitude of  $k$ , the value of the concentration of one substance can be calculated—given that of the others.

In accordance with the law of mobile equilibrium (page 57), chemical equilibrium is shifted in such a way that more and more of the substances, which are formed with the absorption of heat, will be present as the temperature rises.

From this it may be seen that  $K$ , the equilibrium constant, varies with the temperature. At any one temperature it is, however, independent of the absolute value of the concentrations.

Let us apply this mass law to the reaction between water and chlorine writing the latter ionically,



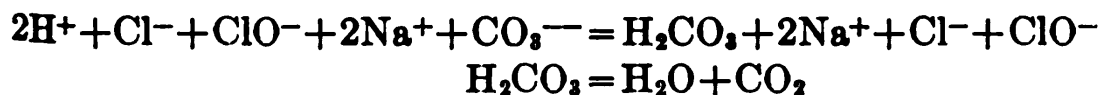
In this  $a$ ,  $b$ , etc., represent the concentrations of the substances just above them. Equilibrium will result when  $c^2de/ab$  has reached a certain definite ratio or

$$\frac{c^2de}{ab} = K$$

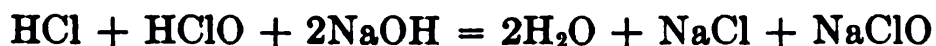
From this it may be easily seen that a decrease in the concentration of one of the substances on the right hand of the equation will decrease the numerator of the constant valued fraction, and this must result in the reaction proceeding from left to right, according to the above equation, until the values of  $a$  and  $b$  have been decreased and those of  $c$ ,  $d$  and  $e$  have been increased sufficiently to restore the original equilibrium value for the fraction. By the addition of any hydroxide, say sodium hydroxide, the concentration of the hydrogen as ion, " $c$ ," may be decreased through the formation of water, and practically all the free chlorine may be consumed. Carbonates, say sodium carbonate  $\text{Na}_2\text{CO}_3$ , or anything else which will use up the hydrogen ion will act in the same way. The carbonates use up the hydrogen ion through the formation of carbonic acid,  $\text{H}_2\text{CO}_3$ , which is not much more broken up into its ions than water. The  $\text{H}_2\text{CO}_3$  is unstable and breaks down into water and gaseous carbon dioxide which escapes from the liquid in bubbles. The equations are



and



The equations written in the ordinary way become



and

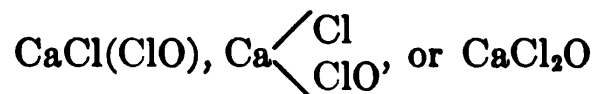


In either case we say that sodium chloride and sodium hypochlorite are formed. The reaction is not usually carried out by saturating water with chlorine and then adding sodium hydroxide,  $\text{NaOH}$ , but by running chlorine into sodium hydroxide solution and the equation is often written,

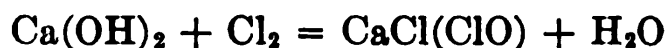


but the action doubtless takes place in the stages indicated above. Other hypochlorites can be made from the hydroxides of the corresponding metals in much the same way by the direct action of chlorine upon the hydroxide, either in solution or in the solid state.

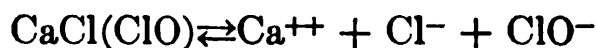
Without question the most important hypochlorite is that of calcium, which in the form of **bleaching powder**, or "chloride of lime," as it is often called, is manufactured by the thousands of tons from chlorine and calcium hydroxide. This bleaching powder is not a pure hypochlorite, but is a mixed salt, half chloride and half hypochlorite, formed by the union of one atomic weight of calcium with an atomic weight of chlorine ion and one of hypochlorite ion. The formula of the salt is given in various ways. Perhaps the most common of these are



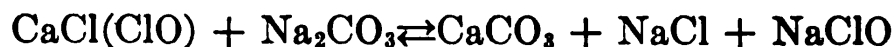
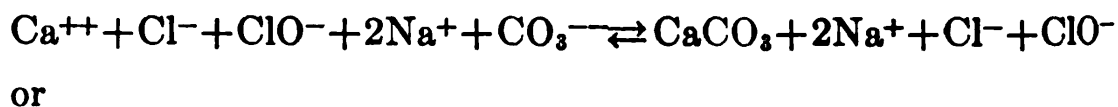
The equation for its formation is as follows,



This bleaching powder is a solid and may be conveniently shipped. It is easily converted into chlorine, into sodium hypochlorite and chloride solution, or into hypochlorous acid. Upon passing into solution in water it acts as though it breaks up into calcium as ion and chlorine and hypochlorite ions.



Upon the addition of sodium carbonate the very slightly soluble calcium carbonate,  $\text{CaCO}_3$ , is precipitated, and sodium, chlorine, and hypochlorite ions are left in solution.



The solution, containing sodium hypochlorite, obtained in this way is very largely used for bleaching cotton and linen goods in the laundries.

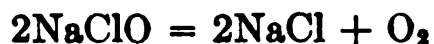
Solutions containing hypochlorite are often formed by elec-

trolysis of solutions of chlorides. Chlorine is liberated at the anode and hydrogen with the simultaneous formation of hydroxide at the cathode. The apparatus is so designed that the chlorine and hydroxide mix almost as soon as formed and hence hypochlorite is produced.

The hypochlorites either alone or when mixed with chlorides are good oxidizing and bleaching agents and also are excellent disinfectants. One very important use for bleaching powder is in the purification of water. This depends upon the fact that very small quantities of the substance will kill typhoid and other pathogenic bacteria without injuring the water for domestic purposes.

The ion  $\text{ClO}^-$  differs markedly in properties from the  $\text{Cl}^-$ . It is for example, a strong oxidizing agent and does not give a precipitate of silver chloride upon the addition of silver nitrate.

**Decomposition of Hypochlorites.**—Hypochlorous acid and its salts are unstable and readily undergo change. Sodium hypochlorite, for example, slowly decomposes into the chloride and oxygen:



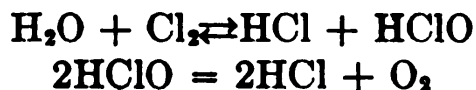
The addition of a small quantity of a cobalt salt results in the formation of a black precipitate of cobaltic hydroxide which acts as a vigorous catalyzer for the decomposition of the hypochlorites. In this way oxygen may be easily obtained from bleaching powder. By adding some cobalt salt to sodium hydroxide solution and then passing in chlorine, a steady stream of oxygen may be obtained. This reaction may be represented as follows:



Mixtures of iron and copper sulfates work in practically the same way as cobalt salts and are used in the technical preparation of oxygen from bleaching powder.

This same decomposition of hypochlorites may be accelerated by light and takes place fairly rapidly in sunlight. The action of light on chlorine water finds an explanation from this fact. The chlorine acts on water, forming hypochlorous and hydrochloric

acids, and the hypochlorous acid then decomposes into oxygen and hydrochloric acid:



or combining,



This ability of hypochlorous acid and its salts to yield oxygen is closely connected with the oxidizing power of these compounds.

In addition to decomposing into oxygen and chlorides, hypochlorites change slowly into chlorates and chlorides. For example, sodium hypochlorite passes into sodium chlorate and chloride, as shown in the following equation:



This change takes place more rapidly when the solution is heated and especially if the solution is acid or contains an excess of chlorine. An alkaline solution of a hypochlorite is fairly stable.

The chlorate formed as described above slowly changes into chloride and perchlorate and the latter in turn decomposes into chloride and oxygen. In order that the reactions shall take place at a reasonable rate the temperature must be far above the boiling-point of water, so to obtain them the dry salts are heated. The equations are



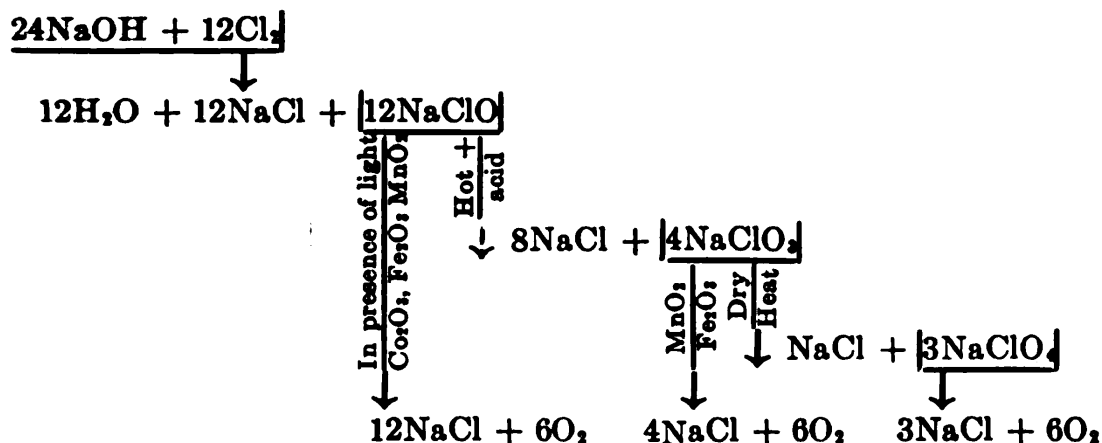
and



The final result is that, after going through these stages, the hypochlorite ultimately is changed completely into chloride and oxygen as is the case with the cold solution in the presence of a cobalt salt. The hypochlorite, chlorate, and perchlorate are unstable substances, while the chloride and oxygen are stable. Except in the presence of cobalt oxide, etc., the system sodium hydroxide and chlorine does not pass directly to its most stable state, sodium chloride, oxygen and water, but goes through a series of stages each more stable than its predecessor until the final stable condition is reached. In this respect, this system seems to be typical of many others which behave similarly. So

generally is this the case that it is described in what is called Ostwald's *Law of Successive Reactions*, which states that a system does not pass directly from the least stable to the most stable state, but does so through a series of steps or stages of gradually increasing stability.

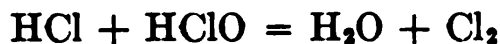
We may represent the successive steps in the transformation of the unstable system, sodium hydroxide and chlorine, into the stable one, sodium chloride, oxygen and water as follows:



The conditions stated along each arrow show the factors which favor the change indicated by the arrow.

This is typical of the changes undergone by other systems of bases and chlorine and gives briefly a general scheme for the preparation of hypochlorites, chlorates, and perchlorates.

**Hypochlorous Acid.**—Hypochlorous acid is very volatile and will stand distillation, consequently it is easily prepared from its salts by the first general method, by adding to a hypochlorite a less volatile acid and distilling. The reaction must be carried out in rather dilute solution since the concentrated acid readily decomposes into water and chlorine monoxide,  $\text{Cl}_2\text{O}$ . Since hypochlorites are difficult to prepare pure, a mixture of hypochlorite and chloride is generally used. Hypochlorous acid  $\text{HClO}$ , is a very much weaker acid than hydrochloric,  $\text{HCl}$  and is almost exclusively formed if a little less acid is added than the amount required to act upon the hypochlorite which is present. It is very important that an excess of acid be avoided since hydrochloric and hypochlorous acids react very rapidly to form chlorine and water.



Bleaching powder is usually used to furnish the hypochlorite and nitric acid is the added acid, care being taken to add it a little at a time and to stir vigorously to avoid any local excess. The equation is

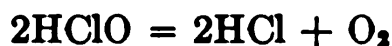


Instead of nitric acid one may use hydrochloric or still better, the very weak boric acid.

The hypochlorous acid formed is volatile and passes over with the first part of the water. It may be still further concentrated by fractional distillation.

**Properties of Hypochlorous Acid.**—The anhydrous acid cannot be prepared, so it is known only in solution. Its concentrated solutions have a yellow color and smell something like bleaching powder. In dilute solutions it is almost colorless. It neutralizes strong bases and forms hypochlorites.

It is unstable and decomposes in several ways. When warmed or exposed to sunlight, it may decompose into hydrochloric acid and oxygen.



or it may change into hydrochloric and chloric acids.



This latter change takes place even in the dark.

In the two cases given above, hypochlorous acid acts like other hypochlorites, but hypochlorous acid differs in one respect from other hypochlorites, and that is, in very concentrated solution it will decompose into water and chlorine monoxide.

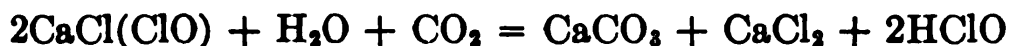


This reaction is reversible and hypochlorous acid is formed by the union of water and chlorine monoxide; consequently the latter is often called hypochlorous anhydride. An **anhydride** is an oxide which will combine with water to form an acid.

As has been mentioned, hypochlorous acid is a powerful oxidizing and bleaching agent, being more active in this respect than other hypochlorites. In fact, there is some little evidence that solutions of hypochlorites owe a part of their bleaching power

to the presence in them of hypochlorous acid. Hypochlorous acid bleaches because it oxidizes and destroys the coloring matters which are usually very complex carbon compounds. Each of these compounds owes its color to a certain definite combination of its constituents, and when this combination is broken up by oxidation or otherwise the color is destroyed. Usually the reaction is too complex to be represented by an equation.

It will be recalled that chlorine was not active as a bleaching agent until the article to be acted upon was moistened. It is probable that it is really the hypochlorous acid formed by the action of the chlorine on the water which does the bleaching. Cotton or linen goods are prepared for bleaching by boiling them in a soap solution for a time to remove grease and oils and then passing them through a dilute solution of bleaching powder and into very dilute sulfuric acid. The last two processes are repeated until the desired results are reached. The goods are then carefully washed to remove the excess of chemicals. The solutions must be very dilute and the operation carried out with care or a large part of the strength of the fabric will be destroyed. Even under the best conditions the cloth is considerably weakened. Wool, silk, and feathers are so greatly altered by chlorine, hypochlorous acid and hypochlorites, that they cannot be bleached by these substances. Hypochlorous acid is formed by the action of carbon dioxide,  $\text{CO}_2$ , upon moist bleaching powder,



and sometimes in bleaching, the goods which have been wet in bleaching powder solution, are simply hung in the air instead of being treated with sulphuric acid. Hypochlorous acid is a powerful disinfectant.

**Chlorine Monoxide.**—Chlorine monoxide or hypochlorous anhydride is usually prepared not by the decomposition of hypochlorous acid which was mentioned above, but by the action of chlorine on mercuric oxide whereby mercuric oxychloride and the chlorine monoxide are formed according to the following equation:



The chlorine monoxide is a yellowish-brown gaseous substance which may be condensed to a liquid boiling at  $+5^\circ\text{C}$ . Its odor

is strong but distinctly different from that of chlorine. Both the gas and the liquid are explosive. The gaseous substance is easily soluble in water. The solution contains hypochlorous acid and therefore this monoxide is also called hypochlorous anhydride.

**Chlorates.**—Chlorates are easily formed by heating solutions of hypochlorites as has been described above. The reactions take place most readily when the solutions are concentrated and slightly acid or contain an excess of chlorine.

Potassium chlorate is the most widely used and important of these salts, although sodium chlorate is taking its place for many purposes because the latter is more soluble.

Potassium chlorate may be prepared by passing an excess of chlorine into a warm concentrated solution of potassium hydroxide. The reaction takes place in stages as in the formation of sodium chlorate, the hypochlorite being first formed. The equations are



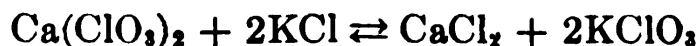
or combining into one and omitting the intermediate stage,



The chlorate is much less soluble than the chloride, so by concentrating the solution and allowing it to cool, the chlorate separates out mixed with only a little of the chloride, which may be removed by a second crystallization. As will be seen from the equation just given, only one-sixth of the somewhat expensive potassium hydroxide is converted into chlorate. The chloride formed at the same time, occurs in nature in large quantities and has a comparatively small value. On a manufacturing scale, this waste is avoided by first preparing calcium chlorate,  $\text{Ca}(\text{ClO}_3)_2$ , by the action of an excess of chlorine upon hot calcium hydroxide.



Potassium chloride is then added to the solution in a little more than the required quantity to react with the calcium chlorate according to the following equation.



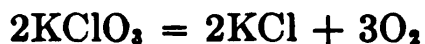
This reaction is reversible and far from complete, but the potassium chlorate is only moderately soluble in cold water, while the potassium chloride is easily and the calcium chloride and chlorate exceedingly soluble; so when the solution is concentrated and cooled, potassium chlorate passes out of solution in the form of crystals. As the potassium chlorate separates from the solution more is formed until finally the greater part of the chlorate has been obtained in the form of the potassium salt.

Chlorates are also very largely made by electrolysis, the process being very much like that for the preparation of hypochlorites, the main difference being that the solution is kept hot and very slightly acid, conditions which it will be recalled are favorable to the change of hypochlorites into chlorates.

**Properties of Chlorates.**—All chlorates are at least moderately soluble in water, and many are so very soluble that they are deliquescent. Potassium chlorate is one of the least soluble of these salts, 100 parts of water at 0°C. dissolve 3.14 parts of this salt. The solubility increases rapidly with rising temperature so that at 100°C. it is approximately eighteen times that at 0°C.

The chlorates all give off oxygen upon being heated and are strong oxidizing agents. Because of this property they are much used in making fireworks, dyes, matches, and explosives. An intimate mixture of sugar,  $C_{12}H_{22}O_{11}$ , and potassium chlorate is sometimes used as a blasting powder, but like practically all other explosives containing chlorates, it is treacherous and dangerous to handle. The addition of a little castor oil makes these explosives safer.

Potassium chlorate, it will be recalled, was used in the laboratory preparation of oxygen. The equation is,



The oxygen so prepared almost always contains a trace of chlorine.

Like sodium chlorate, potassium chlorate if slowly and carefully heated will pass into potassium perchlorate,  $KClO_4$ :

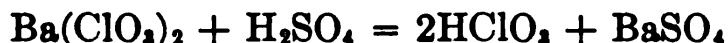


Although chlorates are good oxidizing agents, they are less powerful than the hypochlorites being more stable compounds.

**Preparation of Chloric Acid.**—Chloric acid cannot be distilled without decomposition and therefore cannot be prepared from its salts by the first general method for the preparation of acids. It is made by what is known as the second general method for the preparation of acids from their salts which is briefly as follows: *Add to a solution of a salt of the desired acid another acid which is so chosen that the anion of the added acid shall form a very difficultly soluble compound with the cation of the salt.* This compound is at once formed and passes out of solution, leaving the hydrogen ion of the added acid and the anion of the salt in solution, that is, forming a solution of the desired acid. By careful evaporation, this acid may be then obtained in a pure or at least a more or less concentrated form. Of course the salt to be used and the acid to be added must be very carefully chosen, and just the correct amount of each used. Silver chloride and barium sulfate are among the least soluble of the salts, so silver chlorate,  $\text{AgClO}_3$ , with hydrochloric acid, or barium chlorate,  $\text{Ba}(\text{ClO}_3)_2$ , with sulfuric acid are well adapted for the formation of chloric acid according to the following equations:



and

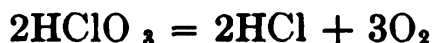


Barium chlorate is much cheaper than silver chlorate, so the latter reaction is the one usually used. The acid solution is filtered from the white precipitate of barium sulfate,  $\text{BaSO}_4$ , and concentrated by evaporation at a temperature below  $40^\circ\text{C}$ . until it contains 40 per cent. of the acid. The dilute solution is colorless while the concentrated has a yellowish tint. It is a strong acid.

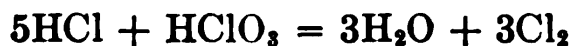
The solution slowly decomposes in a number of ways. It may form perchloric acid,  $\text{HClO}_4$ ,



or break down into hydrochloric acid and oxygen,



The  $\text{HCl}$  so formed then reacts with more  $\text{HClO}_3$  to form chlorine and water,



In addition it may go over into water, chlorine dioxide,  $\text{ClO}_2$ , and oxygen.



When concentrated sulfuric acid is poured on a chlorate, chloric acid is formed, which at once decomposes as shown above. The chlorine dioxide so produced generally explodes spontaneously with such violence that only very small quantities of chlorate should be used.

Chloric acid has found no important application, but its salts are largely used.

**Separation of Salts.**—A solid salt generally separates from its solutions in the form of crystals, and the process of obtaining these is called crystallization. It is very evident from what has been learned, p. 61, that crystals cannot form in an unsaturated solution. In fact the solution must be more than saturated, supersaturated, before they can separate. But in the absence of the solid solute a solution may be considerably supersaturated without crystallization taking place.

Since most substances are more soluble at high temperatures than at low, it is usually very easy to prepare supersaturated solutions by making a saturated solution at a somewhat elevated temperature and then cooling the liquid after the removal of any excess of the undissolved solid. The cooled solution becomes supersaturated and may often be preserved for a long time in this condition by carefully excluding dust which usually contains enough small particles of the solute to bring about crystallization. Generally, however, it will spontaneously deposit crystals as soon as it reaches a certain degree of supersaturation. After the separation has once started it will continue until only so much of the solute remains dissolved as corresponds to its solubility at that temperature. If the supersaturated solution was prepared from crystals of the substance, the process of reobtaining the crystals is known as recrystallization, and is very commonly used in the purification of substances. The process of recrystallization which has just been outlined is especially adapted to the purification of such substances as change their solubility very rapidly with the temperature. Potassium chlorate is a good example. The process is not so well adapted to potassium chloride, and is

of practically no value for things like sodium chloride which are almost as soluble in cold water as in hot (see Fig. 26). In such cases the only way to recrystallize the substances is to evaporate a part of the solvent which will of course cause a corresponding amount of the solute to crystallize. Obviously all of the solvent should not be evaporated since this would leave the salt as impure as before.

When a mixture of salts is dissolved in water, the numerical value of the solubility of each salt is more or less altered but the general relationships are left unchanged. Before any given salt can crystallize, the solution must become supersaturated with that particular salt. As a general rule each salt tends to

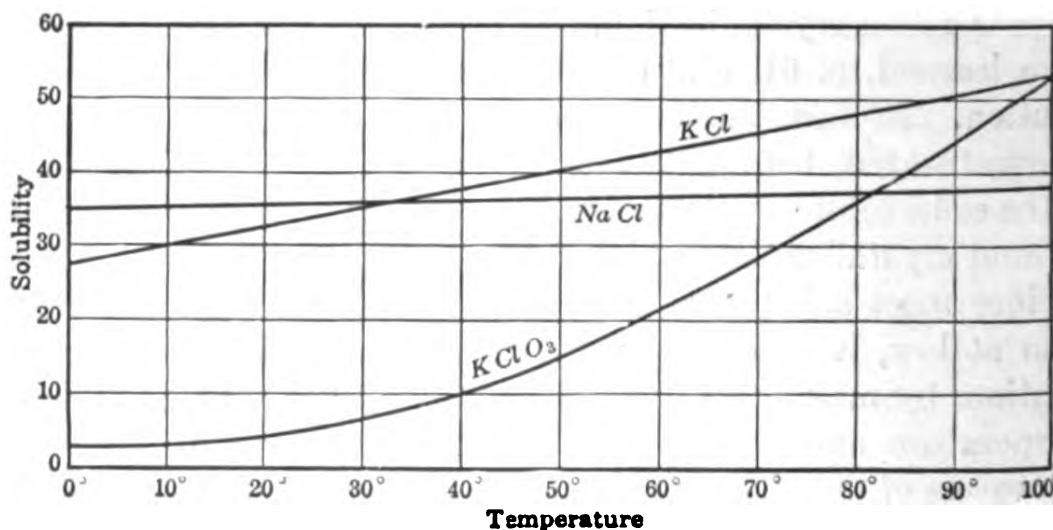


FIG. 26.

crystallize by itself, and if two or more separate at the same time, a mixture of crystals of the salts will be obtained rather than crystals, each of which contains every salt.

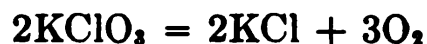
Upon the evaporation of a solution of a mixture of two salts, say for example potassium chloride and chlorate, that salt will separate first whose point of saturation is first exceeded; in this case it is the chlorate at ordinary temperatures, if the salts are present in anything like equal quantities. By removing the crystals as they are formed, they may be obtained in an approximately pure state. Ultimately as the concentration proceeds, the solution will become saturated with the other salt, potassium chloride, and a mixture of crystals will then be formed.

It is not necessarily the least soluble salt which separates first, but that one whose point of saturation is first exceeded. This may easily be the case with the more soluble salt if it is present in relatively large quantities.

**Perchlorates.**—Potassium perchlorate is easily prepared by heating potassium chlorate until it melts and then keeping it at this temperature for some time. A little oxygen is given off and solids begin to form in the molten salt. After a time the whole thing goes solid, although the temperature has not been lowered. The solid so formed is a mixture of potassium chloride, KCl, and potassium perchlorate,  $\text{KClO}_4$ . It is formed according to the following equation,



The evolution of the oxygen had nothing essentially to do with this reaction, and hence is not shown in the equation. It is formed by the side reaction,



The potassium perchlorate,  $\text{KClO}_4$ , is only slightly soluble, so it is easily separated from the potassium chloride, KCl, by finely powdering the mixture and dissolving out the potassium chloride with cold water. A recrystallization of the residue from hot water yields pure potassium perchlorate,  $\text{KClO}_4$ .

The perchlorates are much more stable than the hypochlorites or chlorates. Upon being heated they yield oxygen and chlorides, and may also act as oxidizing agents but are not as active as hypochlorites or chlorates. They are all more or less soluble in water, the potassium salt being one of the least soluble. Some of them are used in matches and fireworks because they are safer than the chlorates.

**Perchloric Acid.**—Perchloric acid is easily formed from the potassium salt by the first general method, using sulfuric acid and cautiously distilling under diminished pressure. Dense white fumes are evolved and a colorless or slightly yellow liquid distills, consisting of pure perchloric acid,  $\text{HClO}_4$ , which condenses in the receiver.

Mixtures of perchloric acid and water act like mixtures of hydrochloric acid and water in that there is a constant boiling

mixture of minimum vapor pressure and maximum boiling-point. This mixture contains 72 per cent. of acid and boils at 203°C. By adding to this constant boiling mixture twice its volume of concentrated sulfuric acid, and distilling, pure perchloric acid may be obtained.

The pure acid is volatile, boiling at 19°C. under a pressure of 1.1 cm. of mercury; and has a density of 1.78. It is a good oxidizing agent and decomposes with great readiness so that when brought in contact with oxidizable substances it generally explodes with violence. When heated under atmospheric pressure it decomposes at 92°C. It dissolves in water with a hissing noise and the evolution of much heat. The aqueous acid of all strengths up to the constant boiling mixture is entirely stable. Unlike hypochlorous and chloric acids, it does not liberate chlorine from hydrochloric acid. It combines with water to form white crystals of perchloric acid monohydrate  $\text{HClO}_4 \cdot \text{H}_2\text{O}$ .

**Perchloric Anhydride.**—Perchloric anhydride,  $\text{Cl}_2\text{O}_7$ , may be prepared by adding to perchloric acid phosphorus pentoxide,  $\text{P}_2\text{O}_5$ , keeping the whole cool by a freezing mixture of ice and salt. After standing for a day the mixture is distilled. The anhydride is colorless and boils at 82°C. It may be distilled under ordinary pressure without danger, but explodes when struck or brought in contact with a flame.

**Chlorine Dioxide and Chlorites.**—As has already been mentioned, one of the ways in which chloric acid decomposes, is into water, chlorine dioxide,  $\text{ClO}_2$ , and oxygen:



Chlorine dioxide is a yellow-brown gaseous substance which may be condensed in a tube cooled with ice and salt. The boiling-point of the liquid is about 10°C. Both the liquid and its vapor are extremely explosive. The vapor explodes when brought in contact with a metal rod heated to a temperature far below redness. The products of the explosion are chlorine and oxygen.

When passed into sodium hydroxide solution, it yields a mixture of sodium chlorate and chlorite,  $\text{NaClO}_3$ .



The chlorites are all unstable substances for which no applications have been found. The acid is known only in dilute solutions. The chlorites appear to stand between the hypochlorites and the chlorates in the order of stability, but the evidence is not entirely conclusive.

**Relative Oxidizing Power.**—It might very reasonably be thought that perchloric acids and chloric acids would be stronger oxidizing agents than hypochlorous acid, because the former contain more oxygen per mole; but this is not the case. Hypochlorous acid is the strongest, and perchloric the weakest. This is connected with the fact that hypochlorous acid is the most unstable and perchloric the most stable of the series.

## CHAPTER XI

### BROMINE, IODINE AND FLUORINE

**General.**—Fluorine, chlorine, bromine and iodine form a group or family of elements which closely resemble one another in their chemical properties and those of the compounds which they form. This group is called the halogen family. From what is to follow, it will be seen that there is a regular change in properties of the halogens and their compounds as the atomic weight of the element increases. It will also be very evident that chlorine, bromine and iodine resemble each other much more closely than they do fluorine. For this reason the discussion of chlorine will be followed immediately by that of bromine and iodine and fluorine will be taken up last.

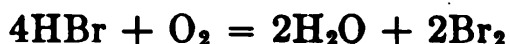
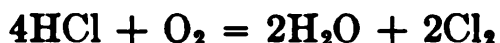
Bromine and iodine are so much like chlorine that a very fair knowledge of their chemistry may be easily obtained by comparison with that of chlorine, noting the many points of resemblance and the few differences. *The root of most of these differences lies in the fact that bromine is liberated from its compounds by weaker oxidizing agents than chlorine, and that iodine is still more readily set free than bromine.*

#### BROMINE

**Occurrence.**—Like chlorine, bromine is never found free, but only in combination, chiefly as bromides of sodium, potassium, and magnesium. It is not nearly as abundant as chlorine, and its compounds are never found in anything like a pure state, but are always mixed with very much larger quantities of chlorides. It is found in sea water, many mineral springs, salt wells, and beds of rock salt. These beds of rock salt have doubtless been formed by the evaporation of sea water, so the presence of bromides in them is not surprising. The bromine content of salt beds differs rather widely, and naturally only the richer deposits are utilized as sources of bromine. The chief bromine-producing localities

are Stassfurt in Germany, and Michigan, Pennsylvania, and West Virginia, in the United States.

**Preparation of the Element.**—From the fact that bromine is more easily liberated than chlorine, it follows that any of the oxidizing agents used in the preparation of chlorine may be employed for bromine, so we may match each of the methods given in the preceding chapter for the preparation of chlorine by a similar one for bromine, as shown by the following equations:



Electrolysis of chlorides and bromides yields respectively chlorine and bromine at the anode.

Of these reactions, that between the bromides, manganese dioxide and sulfuric acid (Fig. 27), is the most important because the bromides are much cheaper and more easily obtained than hydrobromic acid.

In addition to the above, bromine is liberated by a number of oxidizing agents which cannot act on chlorides. The

element chlorine is an oxidizing agent, not as powerful of course as the ones used to set it free, but still powerful enough to liberate bromine as shown in the following equation:

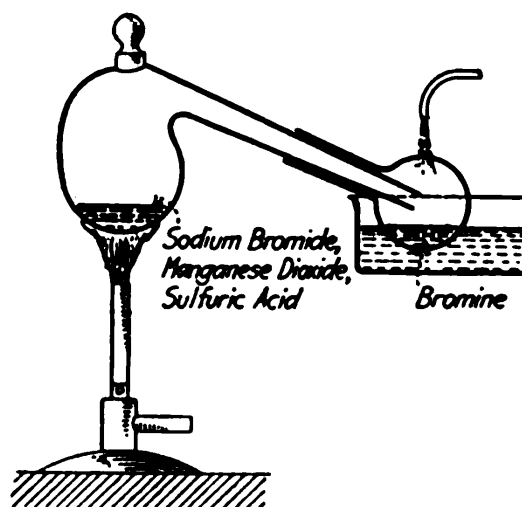
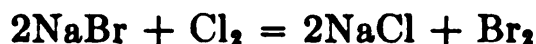


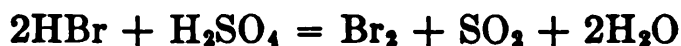
FIG. 27.

The reaction is really between the free chlorine and the bromine ion:



and consequently is an exchange of charges, and yet the liberation of bromine from a bromide is considered oxidation; so this kind of exchange of charges must be counted oxidation and kept in mind until a general definition of oxidation and reduction can be given. It is by this reaction that most of the bromine of commerce is obtained.

Concentrated sulfuric acid is a fairly strong oxidizing agent, strong enough to act on hydrobromic acid, but not on hydrochloric acid.



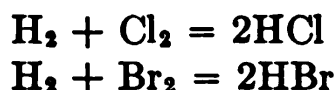
This last action must be kept in mind in the preparation of hydrobromic acid.

**Physical Properties of Bromine.**—Bromine is a dark, brownish-red liquid, which is almost opaque in thick layers, and has a density of 3.19. It boils at 59°C. and freezes at  $-7.3^\circ\text{C}$ . The liquid produces very severe "burns" if it comes in contact with the skin. Bromine is an easily volatile liquid since its vapor pressure at ordinary temperature is about 20 cm. The vapor has a deep red color, an exceedingly stifling odor, and is very irritating to the mucous membrane. The name bromine is derived from the Greek word, *βρωμος*, meaning a stench. The density of the bromine vapors is five times that of oxygen and indicates a molecular weight of 160. Since the atomic weight of bromine (79.92) is half the molecular weight, its formula is  $\text{Br}_2$ . At higher temperatures the molecular weight becomes somewhat less, indicating a partial dissociation of the  $\text{Br}_2$  into Br. Iodine shows this tendency still more strongly.

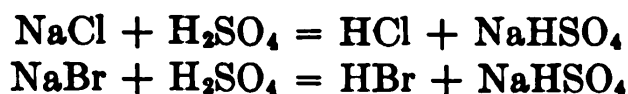
Bromine dissolves in water to the extent of about 3 parts by weight of bromine to 100 parts of water at ordinary temperature. The solution has a yellowish-red color, smells of bromine, and may often be used in the place of the latter when water does not interfere with the reactions. The solubility of bromine is markedly increased if the water also contains some soluble bromides. It is more soluble in carbon disulfide, alcohol, and many organic solvents than it is in water.

**Chemical Properties.**—The chemical properties of bromine are very much like those of chlorine, modified by the fact that it is slower and less intense in its action than the latter. It is a powerful oxidizing agent, though less so than chlorine. It combines directly with hydrogen and most of the other elements forming bromides. With water it forms a hydrate,  $\text{Br}_2 \cdot 8\text{H}_2\text{O}$ , which, in general, is similar to chlorine hydrate.

**Hydrogen Bromide.**—With slight modifications due to the facts mentioned above, that bromine does not combine as vigorously with hydrogen as chlorine does, and that hydrogen bromide is more easily oxidized than hydrogen chloride, practically every method given in Chapter VIII for the preparation of hydrogen chloride may be matched by a corresponding one for hydrogen bromide. This is shown by the following equations.



The mixture of hydrogen and bromine does not explode when exposed to sunlight or an electric spark, as that of hydrogen and chlorine does, but combines fairly rapidly at high temperatures under the influence of platinum as a catalyzer.



In this case dilute sulfuric acid must be used in the preparation of hydrogen bromide because the concentrated acid is a strong enough oxidizing agent to liberate the bromine.

The indirect preparation of hydrogen bromide by the action of bromine upon compounds of hydrogen and carbon corresponds closely to that of hydrogen chloride by the action of chlorine upon these same compounds. For example, bromine and benzene,  $\text{C}_6\text{H}_6$ , react for the formation of hydrogen bromide and monobrombenzene,  $\text{C}_6\text{H}_5\text{Br}$ .

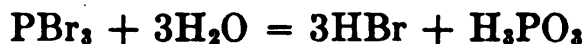


The method which is generally the most convenient for the preparation of hydrogen bromide is by the interaction, at ordinary temperatures, of bromine, red phosphorus and water (Fig. 28). The action takes place in steps. First the bromine and the

phosphorus combine for the formation of phosphorus tribromide,  $\text{PBr}_3$ .



This then reacts with water to form phosphorous acid,  $\text{H}_3\text{PO}_3$ , and hydrogen bromide,  $\text{HBr}$ .



Hydrogen chloride might be prepared in an analogous way, but the action is very violent and the method is not so cheap and convenient as that from salt and sulfuric acid.

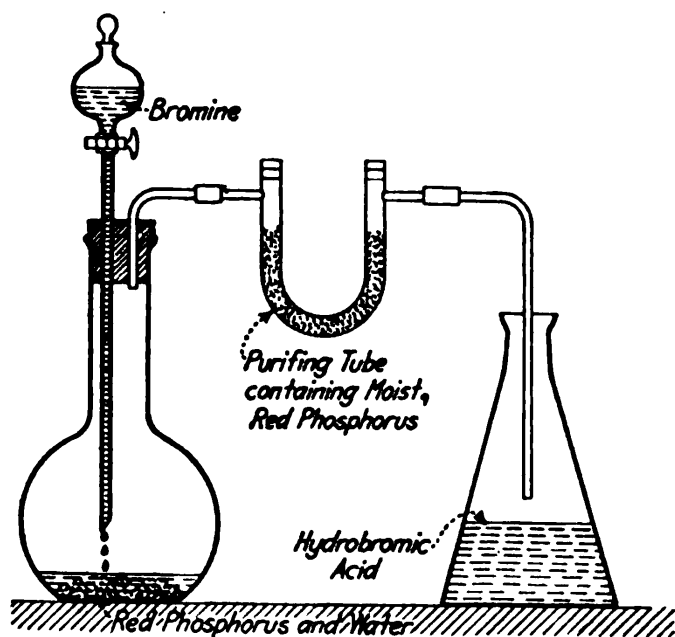
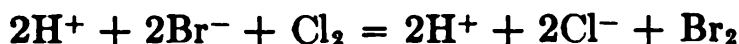


FIG. 28.

**Properties of Hydrogen Bromide.**—Like hydrogen chloride, hydrogen bromide is a colorless gaseous substance at ordinary temperatures. Its critical temperature is  $91^\circ\text{C}$ . At low temperatures it condenses to a colorless liquid, boiling at  $-68.5^\circ\text{C}$ . and freezing at  $-86^\circ\text{C}$ . The gaseous density of hydrogen bromide shows that it has a molar weight of 81, and the formula  $\text{HBr}$ . It is very soluble in water, 600 volumes of hydrogen bromide to one of water, and fumes upon contact with moist air. Like hydrogen chloride, it forms a maximum boiling solution with water. The composition of this is 48 per cent. hydrogen bromide, and it boils at  $126^\circ\text{C}$ .

Like hydrogen chloride, dry hydrogen bromide is a rather indifferent substance, but when in solution in water it is as

highly acid as hydrochloric acid and its solution is known as hydrobromic acid. It acts upon metals much as other acids do, forming hydrogen gas and solutions of the bromides of the metals. Speaking in terms of the ionic theory, solutions of hydrobromic acid and bromides contain the bromine ion  $\text{Br}^-$ . The properties of this ion are very much like those of the chlorine ion. It is colorless, forms a very difficultly soluble compound with silver, silver bromide,  $\text{AgBr}$ , which is less soluble than silver chloride and has a slight yellow color. The liberation of bromine from the bromine ion by chlorine is the easiest way to distinguish the bromine ion from the chlorine ion. The equation for the reaction is

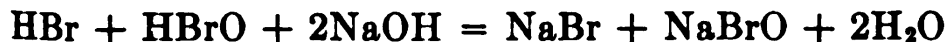


The free bromine colors the solution yellowish-red. If the solution be shaken with a little carbon bisulfide, the latter takes up most of the bromine from the water and becomes highly colored. This makes a very delicate test for bromine.

**Oxygen Compounds of Bromine.**—No one has, so far, succeeded in preparing oxides of bromine, perbromic acid, or perbromates, but hypobromous acid,  $\text{HBrO}$ , and bromic acid,  $\text{HBrO}_3$ , and their salts are well known. The reactions for their preparation are exactly analogous to those for the corresponding chlorine compounds. The first step is the reversible reaction between bromine and water for the formation of hydrobromic and hypobromous acids,



When equilibrium results, the concentrations of the acids are even less than in the corresponding reaction for chlorine. The addition of sodium or potassium hydroxides will destroy the equilibrium by neutralizing the acids and cause the reaction to run toward the right until nearly all the bromine has been used up, and there results a solution of a mixture of the bromide and hypobromite salts.



or, combining the two equations



The change of the hypobromites into bromates takes place even more rapidly upon heating, than the corresponding change of the hypochlorites. The equation is



Hypobromous acid is so unstable that even a dilute solution of it is hard to make and soon decomposes. Bromic acid may be made from its salts by the second general method for the preparation of acids, or by the action of hypochlorous acid upon bromine water:

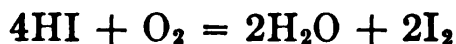


### IODINE

Iodine occurs in nature almost exclusively in combination, chiefly as iodides and iodates. It has, however, been found free in waters of certain mineral springs, having been liberated from hydriodic acid by the action of dissolved oxygen. This is in line with the fact that iodine is more easily liberated by oxidizing agents than either chlorine or bromine.

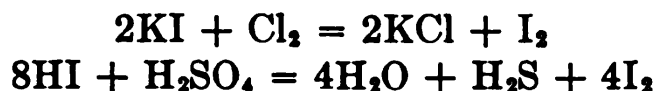
Iodides are found in sea water, but in much smaller quantities than bromides. Fairly large quantities of iodates, chiefly that of sodium, are found in the Chile saltpeter beds, and the greater part of the iodine of commerce is obtained from the mother liquor left in the purification of this crude sodium nitrate. The other source of iodine is from ashes of certain seaweeds gathered off the coasts of Scotland and Ireland. They were formerly the main source of iodine, and it was in their ashes that the element was discovered.

**Preparation of the Element.**—Iodine may be liberated from iodides by any of the oxidizing agents used for chlorine or bromine, and by some others in addition which are too feeble to serve in the other cases. A few of the equations are given below; others may be easily written by simply substituting the symbol "I" for "Cl" or "Br" in the corresponding equations for these elements:



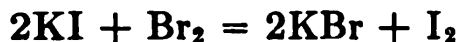
The last reaction is very commonly used (Fig. 29).

Like bromine, iodine may be liberated by the action of chlorine or strong sulfuric acid upon hydriodic acid or iodides:



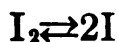
Hydriodic acid is oxidized even more readily by sulfuric acid than hydrobromic is, and hence it is not possible to prepare hydriodic acid by the distillation of an iodide with sulfuric acid.

Just as free chlorine will liberate free bromine from hydrobromic acid or bromides, so bromine will set iodine free from the corresponding iodine compounds:



**Physical Properties of Iodine.**—At ordinary temperatures chlorine is gaseous, bromine liquid, and iodine solid; this shows a regular change in the physical state as the atomic weight increases. Iodine crystallizes in large rhombic plates, having a steel gray color and an almost metallic luster. It melts at  $114^\circ\text{C}.$ , and boils at  $184^\circ\text{C}.$  The vapor has a beautiful violet color which is so strong that it can be seen in a bottle containing iodine at ordinary temperatures, although the vapor pressure of iodine at such temperatures is very low.

The vapor density of iodine at ordinary pressures and temperatures below  $700^\circ\text{C}.$  shows a molecular weight of 254. The atomic weight of iodine is 126.92, hence the formula for iodine under these conditions is  $\text{I}_2$ . If the temperature be raised above  $700^\circ\text{C}.$  the molecular weight gradually decreases until at  $1,700^\circ\text{C}.$  it becomes constant again at 127 corresponding to the formula  $\text{I}$ . Rise in temperature then above  $700^\circ\text{C}.$  has caused a reversible dissociation of  $\text{I}_2$  into  $\text{I}$ .



The color of  $\text{I}$  is different from that of  $\text{I}_2$ , and doubtless if the high temperature did not interfere with its study  $\text{I}$  would be found to be a strikingly different substance from  $\text{I}_2$ .

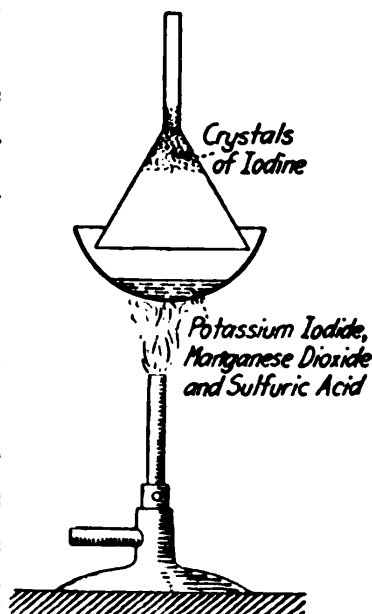


FIG. 29.

Iodine is but very slightly soluble in pure water, imparting to it a brownish color. It is much more soluble in alcohol, chloroform, and carbon disulfide than in water. The alcoholic solution is brown, while that in chloroform or carbon disulfide has the violet color of the vapor. Free iodine will dissolve in solid starch forming a solid solution having a strong blue color. This may be used as a very delicate test for either starch or iodine. In the latter case, it is carried out as follows: a suspension of finely divided starch in water is prepared by pouring boiling water over starch rubbed to a cream with a little water. Some of this is added to the solution suspected to contain iodine. If the latter is free, the strong blue color of the starch iodide solution at once appears. If the iodine is not free, it is liberated by the cautious addition of a little chlorine water.

**Law of Distribution.**—As mentioned above, iodine is much more soluble in carbon disulfide than in water. Carbon disulfide and water are not appreciably soluble in each other, and when brought together form two liquid layers, the carbon disulfide at the bottom. If now, some iodine be introduced, it will dissolve both in the water and the carbon disulfide, but to a far larger concentration in the latter. In fact, when equilibrium results it will be found that the weight of iodine per cubic centimeter in the carbon disulfide is 600 times that per cubic centimeter in the water.

This is an example of the phenomena described by the law of distribution which states that: *When two immiscible liquids are brought in contact with a third substance, soluble in each, this third substance distributes itself between the two solvents until its concentration in the one solvent bears a certain constant ratio to its concentration in the other.* In this case, the ratio of the concentration in the carbon disulfide to that in water is 600 : 1. Some substances have higher molecular weights in certain solvents than in others and this law holds only when the molecular weight of the third substance is the same in each of the solvents.

**Chemical Properties of Iodine.**—The chemical properties of iodine are very much like those of chlorine and bromine except that it is much less active and is not so strong an oxidizing agent. It combines directly with hydrogen and many other elements for the formation of iodides. It does not form a hydrate with water.

Iodine is much more soluble in solutions of iodides than in pure water. In many ways the solution acts as though the iodine were free, in others, it behaves as if it were in combination. This is explained by assuming the existence in the solution, of a complex ion,  $I_3^-$  formed by the reversible reaction shown below:



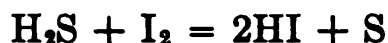
**Hydrogen Iodide.**—The slight differences in the methods for the preparation of hydrogen iodide from those for hydrogen chloride and bromide are due mainly to the fact that it is still less stable and more easily oxidized than the latter. It may be made by the direct combination of the elements. The action is, however slow, reversible, and far from complete. It is catalyzed by platinum, but this simply brings about the equilibrium quicker without changing the composition of the equilibrium mixture. At 400°C., 80 per cent. of a mixture of equal volumes of hydrogen and iodine gases will be converted into hydrogen iodide, or 20 per cent. of pure hydrogen iodide will be decomposed; and this gaseous mixture will remain unchanged in composition so long as it is kept at this temperature. If increasing pressure is put upon this system, no change will follow because as shown in the equation



there is no change in volume as the reaction proceeds.

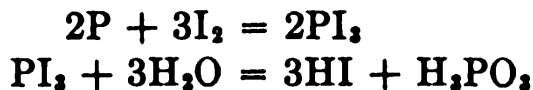
As mentioned above, the preparation of hydrogen iodide by the action of sulfuric acid upon sodium iodide is excluded because of the oxidizing action of the sulfuric acid. By using phosphoric acid instead of sulfuric, hydrogen iodide may be prepared by this method.

It may be made by the action of iodine upon hydrogen compounds. An aqueous solution of hydrogen iodide may be easily obtained by passing hydrogen sulfide into a suspension of iodine in water:



The most common method for the preparation of hydrogen iodide is by the interaction of iodine, phosphorus and water.

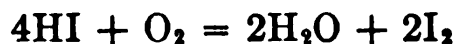
Phosphorus tri-iodide is first formed and then decomposed by water giving hydrogen iodide and phosphorous acid:



This is analogous to the best method for the preparation of hydrogen bromide.

**Physical Properties.**—Hydrogen iodide as a colorless gaseous substance much heavier than air as its molecular weight is 128. It may be condensed to a slightly yellowish liquid, boiling at  $-36^\circ\text{C}$ . and freezing at  $-51^\circ\text{C}$ . Hydrogen iodide is very soluble in water; the solution saturated at  $0^\circ\text{C}$ . contains 200 parts by weight of hydrogen iodide to 100 parts of water. Like hydrogen chloride and bromide, it forms a maximum boiling mixture with water which boils at  $128^\circ\text{C}$ . and contains 57 per cent. hydriodic acid.

**Chemical Properties.**—Hydrogen iodide is the least stable of the hydro-halides and is so easily oxidized that it is an excellent reducing agent. It burns in oxygen, reacts with chlorine with a flash of light and the formation of hydrogen chloride and free iodine. The liquid is a non-conductor of electricity and is inactive chemically. But the solution in water, hydriodic acid, is an excellent conductor of electricity and is a strong acid, being as active as hydrochloric acid solution containing an equal number of gram moles per liter. When a colorless solution of hydriodic acid is exposed to the air it takes up oxygen, quickly turns brown, and finally deposits crystalline iodine. The equation is as follows:



It is this reaction which gives the iodine in the rare cases mentioned above in which it occurs free in nature.

**Oxygen Compounds of Iodine.**—The oxygen compounds of iodine are, in general, much more stable than those of bromine. They are formed in analogous ways to the corresponding compounds of chlorine. The halogen first reacts with water and a base to give an iodide and hypoiodite. The hypoiodites are even more unstable than the hypobromites, and very quickly pass over into the iodides and iodates.

It will be recalled that iodine occurs in nature largely as sodium iodate in the Chile saltpeter beds.

Iodic acid may be prepared from iodates by the second general method, but is more readily obtained by the action of nitric acid upon iodine, as shown in the following equation:

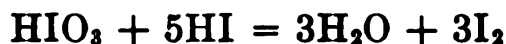


$\text{NO}_2$  is called nitrogen peroxide.

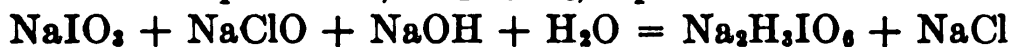
Iodic acid is a stable substance which crystallizes from its very concentrated solutions in lustrous crystals which are extremely soluble in water. The solution is a strong acid. By carefully heating the crystals, they decompose into water and iodine pentoxide,  $\text{I}_2\text{O}_5$ ,



The action is reversible so that the pentoxide is also called iodic anhydride. Iodic acid is a fairly strong oxidizing agent and rapidly reacts with hydriodic acid to form iodine.



**Periodates and Periodic Acid.**—When sodium hypochlorite in alkaline solution acts upon sodium iodate, rather difficultly soluble sodium periodate,  $\text{Na}_2\text{H}_2\text{IO}_6$ , separates out:



This is the disodium salt of orthoperiodic acid,  $\text{H}_5\text{IO}_6$ , which may be easily prepared by the second general method for the preparation of acids. As will be seen, this does not correspond very closely with perchloric acid,  $\text{HClO}_4$ . By long and careful heating to  $100^\circ\text{C}$ . in a vacuum the ortho acid,  $\text{H}_5\text{IO}_6$ , loses water and passes over into the meta acid,  $\text{HIO}_4$ .

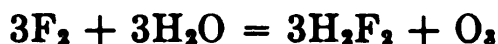
**Oxides of Iodine.**—Iodine forms two oxides, the tetroxide,  $\text{I}_2\text{O}_4$ , and the pentoxide,  $\text{I}_2\text{O}_5$ ; the latter is iodic anhydride.

## FLUORINE

The atomic weight of fluorine is 19, which is smaller than that of chlorine, and hence, logically, it should have been considered first; but, as said before, its properties are not as typical of the halogens as are those of chlorine, and consequently it was left until this point.

**Occurrence.**—Fluorine never occurs free in nature, in fact it is one of the most difficult of the elements to liberate. It is generally found as calcium fluoride (fluor spar),  $\text{CaF}_2$ . Two other fairly common compounds are cryolite,  $\text{Na}_3\text{AlF}_6$ , and apatite,  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ . These are all difficultly soluble, while the most abundant of the naturally occurring compounds of the other halogens have been easily soluble.

**Preparation.**—As we passed from chlorine through bromine to iodine, it was noted that it became easier and easier to oxidize the compounds, and so to liberate the elements, as the atomic weight increased. This would lead us to expect that fluorine, the halogen with the smallest atomic weight, would be the hardest to oxidize, and this is found to be true; in fact there is no oxidizing agent powerful enough to set the fluorine free. There remains then only one method for its preparation, electrolysis of a compound. Water must be absent because fluorine and water immediately react with the formation of hydrogen fluoride and ozone,



Anhydrous liquid hydrogen fluoride is almost a non-conductor of electricity, but it dissolves potassium acid fluoride readily; this salt dissociates into ions and the solution becomes a conductor. Fluorine is given off at the anode and hydrogen at the cathode. Possibly potassium is first liberated, and then reacts with the hydrogen fluoride,



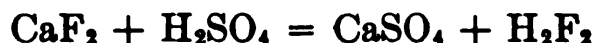
The electrolysis is carried out in a copper U-tube cooled to  $-23^\circ$  using platinum-iridium electrodes.

**Physical Properties.**—Fluorine is a gas having a greenish-yellow color much like that of chlorine only less intense. It liquefies at low temperatures, boils at  $-186^\circ$  and freezes at  $-223^\circ$ . Because of the very great activity of fluorine, it is difficult to determine its density; but the molecular weight evidently is not far from 38, and since the atomic weight is 19 the formula is  $\text{F}_2$ .

**Chemical Properties.**—Fluorine combines with all the elements except oxygen, nitrogen, chlorine and the members of the argon group. Hydrogen fluoride is an especially stable compound and is instantly formed when fluorine is brought in contact with hydro-

gen even at a temperature of  $-252^{\circ}$  or with almost any hydrogen compound at ordinary temperatures. The reaction with water has been noted above. Fluorine and hydrogen chloride react for the liberation of chlorine; of course, it will react even more readily on hydrogen bromide and hydrogen iodide.

**Hydrogen Fluoride.**—Hydrogen fluoride containing a little water may be easily prepared by distilling a fluoride, usually that of calcium, with sulfuric acid:



Here, of course, there is no difficulty caused by the oxidation of the hydrogen fluoride. But there is a complication due to the fact that hydrogen fluoride will readily attack glass, and hence the operation must be carried out in platinum or lead retorts. The anhydrous acid may be easily prepared by heating acid potassium fluoride in a platinum retort.



**Physical Properties.**—Hydrogen fluoride is a clear colorless liquid boiling at  $19^{\circ}$ . This is exceptionally high when compared with hydrogen chloride, etc. It dissolves readily in water, and like the other hydrogen halides forms a constant boiling mixture with water. This contains 35 per cent. hydrogen fluoride and boils at  $120^{\circ}\text{C}$ . The density of hydrogen fluoride vapor, at temperatures but little above its boiling-point, shows a molecular weight of 40, corresponding to  $\text{H}_2\text{F}_2$ ; at higher temperatures the density decreases, and from the boiling-point of water upward the molecular weight is 20 and the formula  $\text{HF}$ . The existence of the compound  $\text{H}_2\text{F}_2$  is an important point of difference from the other hydrogen halides.

The formula  $\text{H}_2\text{F}_2$  indicates a dibasic acid; that is, one a mole of which can neutralize two moles of sodium hydroxide. This is confirmed by the existence of potassium acid fluoride,  $\text{KHF}_2$ , and others of the same type. The neutral salt,  $\text{K}_2\text{F}_2$  or  $\text{KF}$ , is also well known.

The most interesting property of hydrogen fluoride is its action on glass and other silicon compounds. When it acts on glass which contains silicates of sodium and calcium, gaseous silicon fluoride,  $\text{SiF}_4$ , and fluorides of sodium and calcium together with water are formed:

Use is made of this for etching designs on glass. The glass is first coated with wax, the design is scratched through, and then the whole exposed to the vapor or a solution of hydrogen fluoride. Because of this action, it is of course impossible to keep hydrofluoric acid in glass, but it may be kept in wax or gutta-percha bottles. The commercial acid is stored and shipped in lead containers.

The action of hydrofluoric acid on glass is not due to its being an especially strong acid, because when we come to examine its action upon metals we find that a solution containing 20 gm. of hydrofluoric acid in 1,000 gm. of water will act much more slowly on a given piece of zinc than will a solution containing 36.47 gm. of hydrochloric acid in the same amount of water; and yet each solution contains the same amount of hydrogen which is capable of being replaced by a metal. The electrical conductivity of a normal hydrofluoric acid solution is much smaller than that of normal hydrochloric acid and this indicates that hydrofluoric acid is much weaker than hydrochloric.

The following table gives in a condensed form a summary of the more important of the properties of the halogens.

Formula of element	F <sub>2</sub>	Cl <sub>2</sub>	Br <sub>2</sub>	I <sub>2</sub> , I
Atomic weight.....	19	35.46	79.92	126.92
Physical state at ordinary temperature.	gas	gaseous	liquid	solid
Boiling-point.....	-186°	-33.6°	+59°	+184°
Freezing-point.....	-223°	-102.0°	- 7.3°	+114°
Color.....	light yellowish green	yellowish green	Brown red	Gray (vapor violet)
Oxidising agent.....	strongest	very strong	strong	weak
Hydrogen compounds.....	H <sub>2</sub> F <sub>2</sub> - HF	HCl	HBr	HI
Physical state.....	gaseous	gaseous	gaseous	gaseous
Boiling-point.....	+19°	- 83°	-68.5°	-36°
Freezing-point.....	-92.3°	-112°	-86°	-51°
Color.....	colorless	colorless	colorless	colorless
Solution in water.....	weak acid	strong acid	strong acid	strong acid
Action toward oxidizing agents...	unchanged	oxidised by strong	rather easily oxidised	very easily oxidised
Heat of formation Gaseous.....	161Kj.	92Kj.	35Kj.	-26Kj.
Heat of formation dissolved.....	205Kj.	165Kj.	118Kj.	+55Kj.
Heat of Neutralization NaOH...	68Kj.	57Kj.	57Kj.	57Kj.
Oxyacids.....	none	HClO HClO <sub>2</sub> HClO <sub>3</sub> HClO <sub>4</sub>	HBrO ..... HBrO <sub>3</sub> .....	HIO ..... HIO <sub>3</sub> H <sub>5</sub> IO <sub>6</sub>

This table shows that there are regular changes in a number of the properties of these elements as the atomic weight increases. For example the boiling- and melting-points of the elements rise as the atomic weight increases. The student will gain considerable information if he follows the other properties of these elements through in the same way.

Hydrogen fluoride has an abnormally high boiling-point. In this connection, it is significant that it alone of the hydrohalides ionizes solutes and that other ionizing solvents boil higher than their inactive analogues.

**Hydrolysis.**—Salts of weak acids or of weak bases when in solution in water act in a very peculiar manner. Their solutions are not neutral as are those of the salts of strong acids and bases, but the salts of weak acids give alkaline, while those of weak bases give acid reacting solutions. Since the salts themselves do not contain either the hydroxyl or the hydrogen ions, which give the solutions their reactions, the question of the source of these ions is one which calls for some little explanation. Evidently they must have come from the water. But why should the hydroxyl ion appear in a solution of a salt of a weak acid, and the hydrogen ion in the salt of a weak base when neither is prominent in a solution of a salt of a strong acid and base? The theory of electrolytic dissociation furnishes a satisfactory explanation.

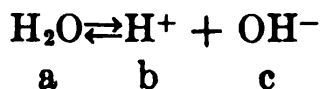
Pure water is a very poor conductor of electricity but it is not an absolute non-conductor. Its conductivity has been measured and indicates that water itself is dissociated to a slight extent so that 1 gm. of hydrogen and 17 gm. of hydroxyl as ion are present in eleven million liters of water. Expressing the concentration in terms of the number of gram ions per liter, the concentration of each of these substances is the same and they balance each other in their action on litmus.

Reactions between substances in the ionic condition tend to take place in such ways that the concentrations of the ions are reduced, either through the formation of substances which pass out of solution or those which are but slightly dissociated.

When a salt of a weak acid and a strong base, say sodium hypochlorite, is dissolved in water, there are present side by side sodium, hypochlorite, hydrogen, and hydroxyl ions. Hypo-

chlorous acid is a very weak acid, and hence, but slightly dissociated, while sodium hypochlorite is highly dissociated. There is then a chance for a decrease in the ions by the union of the hydrogen and the hypochlorite ions, and this they are assumed to do to a certain extent. The solution would then contain sodium as ion, some hypochlorite, enough hydroxyl to make up for the hypochlorite ion which combined with hydrogen as ion, and undissociated hypochlorous acid. The undissociated hypochlorous acid of course does not redden litmus, while the hydroxyl ion turns litmus blue. So the solution reacts alkaline and it is evident that a salt of any other weak acid should act in the same way.

When the hydrogen ion combines with the anion of the weak acid, not only is the hydroxyl left unbalanced in its action upon litmus, but the concentration of the hydroxyl increases. This comes from more of the water's breaking up in an effort to keep up the concentration of the hydrogen. The equation for the ionization of water is



Letting a, b and c represent the concentrations of the water, hydrogen and hydroxyl ions respectively, the Mass law equation becomes

$$\frac{bc}{a} = \text{constant}$$

Now a is constant because it stands for the concentration of a homogeneous liquid, and hence the product bc is constant and as b decreases c must increase.

Salts of weak bases and strong acids react acid because of the combination of the cation of the salt with the hydroxyl of the water with the formation of the undissociated base, thus leaving the hydrogen as ion in excess.

The phenomena which we have just been discussing are included under the name of hydrolysis. Speaking in terms of the ionic theory we may say that hydrolysis consists in the formation of an undissociated acid or base by the action of water upon a salt of a weak acid or base.

Solutions of salts of strong acids and bases are neutral, because under these conditions there is no tendency for either hydrogen or hydroxyl to combine with an ion of the salt; so these salts do not hydrolyze.

### VALENCE

The formulas of some of the principal hydrogen compounds of the non-metallic elements are given in the following table:

HF	H <sub>2</sub> O	H <sub>2</sub> N	H <sub>4</sub> C
HCl	H <sub>2</sub> S	H <sub>3</sub> P	H <sub>4</sub> Si
HBr	H <sub>2</sub> Se	.....	.....
HI	H <sub>2</sub> Te	.....	.....

Several of these compounds have not been studied as yet, but they are introduced here simply to show the different types of combination. H<sub>2</sub>S is hydrogen sulfide, H<sub>2</sub>Se hydrogen selenide, H<sub>2</sub>Te hydrogen telluride, H<sub>2</sub>N or NH<sub>3</sub> ammonia, and H<sub>3</sub>P phosphine, H<sub>4</sub>C or CH<sub>4</sub> marsh gas, H<sub>4</sub>Si silicon hydride.

From this table it may be seen that these compounds fall naturally into four groups according to the number of atomic weights of hydrogen which unite with one atomic weight of the other element. *Each element is considered to have a certain combining power or valence which is measured by the number of atomic weights of hydrogen or of an equivalent substance with which one atomic weight of that element can unite to form a compound.* This number is called the valence of the element. From the definition of valence, it follows that in the compounds given in the above table, fluorine, chlorine, bromine, and iodine are monovalent; oxygen, sulfur, selenium and tellurium divalent; nitrogen and phosphorus trivalent; while carbon and silicon are tetravalent. Hydrogen is our standard substance for measuring valence and is taken to have a valence of one or to be monovalent. Sometimes an element does not combine with hydrogen, and then of course it is not possible to work out the valence from the hydrogen compound, and in this case we must resort to some other method. One of these is to take a compound with some equivalent substance. *An equivalent substance is a substance one atomic weight of which can unite with, replace, or be replaced by, one atomic weight of hydrogen.*

An atomic weight of sodium replaces one atomic weight of hydrogen in the compound hydrogen chloride forming sodium chloride,  $\text{NaCl}$ , and is therefore monovalent; also one atomic weight of silver is replaced from silver chloride,  $\text{AgCl}$ , by one atomic weight of hydrogen, re-forming hydrogen chloride, therefore, silver is monovalent. Chlorine then in chlorides is determined to be monovalent: directly because it was originally combined with one atomic weight of hydrogen in hydrogen chloride; indirectly because it is combined with one atomic weight of the monovalent substances silver and sodium. Because chlorine in chlorides is monovalent, phosphorus in phosphorus trichloride,  $\text{PCl}_3$ , is trivalent, while in the pentachloride,  $\text{PCl}_5$ , it must be pentavalent. It is not necessary, however, that we take a compound with a substance exactly equivalent to one atomic weight of hydrogen; for once we have established the valence of any given element, it may in turn be used to measure that of others. One atomic weight of oxygen is united with two atomic weights of hydrogen in the compound water, hence oxygen is divalent and is commonly used as a standard for determining valence. Take for example, phosphorous trioxide,  $\text{P}_4\text{O}_6$ ; the six atomic weights of oxygen have together a valence of twelve, which is divided between the four atomic weights of phosphorus, showing that each atomic weight of the latter has a valence of three. In the pentoxide,  $\text{P}_2\text{O}_5$ , the valence of the five oxygens is ten, which is divided between the two of phosphorus; and therefore in this compound the phosphorus has a valence of five, as in the pentachloride.

The examples just given show that the valence of an element is not a fixed constant. However, the number of valences belonging to any one element is generally small. Nitrogen has an unusually large number of valences, as may be seen from the following list of its oxides,  $\text{N}_2\text{O}$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}_3$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}_5$ . In these it varies from monovalent to pentavalent. Comparatively few elements have more than two valences so that these properties are not difficult to learn, and they are of great assistance in the formulation of compounds.

**Equivalent Weights.**—The conception of valence enables us to get easily another useful conception, that of equivalent weight. This is the number of parts by weight of an element

which will combine with, replace or be replaced by 1.008 parts by weight of hydrogen, or 8 parts of oxygen. Or it may be defined as the atomic weight of the element divided by its valence. For example, the equivalent weight of sulfur in hydrogen sulfide is  $32.06\frac{1}{2}$ ; of nitrogen in ammonia is  $14.01\frac{1}{3}$ ; of carbon in marsh gas is  $12\frac{1}{4}$ . From the second form of the definition of equivalent weight, it is evident that an element has as many equivalent weights as it has valences.

These equivalent weights are like the atomic weights in many respects, except that they represent directly without any multiple the proportions by weight in which the elements combine.

## CHAPTER XII

### SULFUR

**General.**—Sulfur is an element which has been known since prehistoric times. It occurs fairly abundantly in nature, both free and in compounds. The free sulfur is generally found in volcanic regions, but several deposits of non-volcanic sulfur are known, notably those of Louisiana which now furnish most of the sulfur used in the United States together with large quantities for export. In combination, sulfur occurs chiefly in the form of sulfates, such as gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , Glauber salts,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , and Epsom salts,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , and as sulfides, pyrite,  $\text{FeS}_2$ , zinc blende,  $\text{ZnS}$ , and galena,  $\text{PbS}$ . It is present in combination in many portions of the animal and plant organisms.

In many of its chemical properties, sulfur shows a rather close relationship to oxygen. Like oxygen it is able to assume allotropic forms, and is somewhat remarkable for the large number of such modifications which are known to exist, two and probably more crystalline modifications, two liquid, and at least two gaseous forms.

**Extraction of Sulfur.**—Most of the sulfur from volcanic sources comes from Sicily where it is found in large quantities mixed with limestone, gypsum, celestite and other minerals. The sulfur is extracted from the ore by heating in oven-like kilns or cells made of masonry. The greater part of the heat is furnished by burning coke which is mixed with the ore and charged into the cells. Of course, part of the sulfur burns. Economy of fuel is secured by arranging the cells in batteries of two or more and passing the gases from the one in action into a freshly charged cell in order that the waste heat from the first may warm the charge in the second. The sulfur melts and runs down to the floor of the cell from which it is drawn off and cast into conical wooden moulds forming the roll sulfur or brimstone of commerce. In some more recent installations the sulfur is extracted by melt-

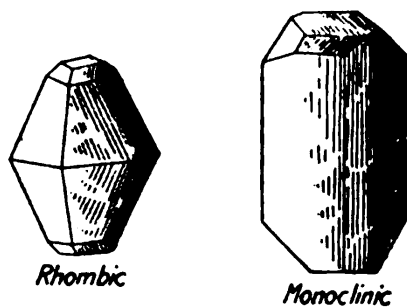
g it out with high-pressure steam. This method is being used with success in some rather recently developed mines in Mexico.

In Louisiana, the sulfur is obtained by drilling down about 100 ft. to the sulfur-bearing deposits and forcing down into the holes water heated to a temperature of  $168^{\circ}$  which is far above the melting-point of sulfur ( $120^{\circ}$ ). The water must, of course, be under pressure of about seven atmospheres to reach this temperature. The sulfur melts and collects at the bottom of the hole; from there it is pumped out by compressed air. The sulfur can be obtained in this way very cheaply, and is more than 99.5 per cent. pure. A single well often yields 500 tons of sulfur per day and the entire mine has produced 122,000 tons in two months which is more than the world's consumption for that period. The production of sulfur in the United States in 1914 was 328,000 long tons.

**Purification of Sulfur.**—When it is necessary to purify roll sulfur, the process of distillation is employed. The sulfur is boiled in iron retorts and the vapor is condensed in large brick chambers. At first when the walls of the chamber are cool, the sulfur condenses in the form of a rather fine powder, and is put on the market under the name of flowers of sulfur. When the chamber becomes heated from the heat of condensation of the sulfur, the latter collects in the form of a liquid and is drawn off into moulds as before.

**Crystalline Forms of Sulfur.**—Crystals of rhombic (Fig. 30) or  $\alpha$  sulfur are found in nature and may be easily prepared by dissolving sulfur in carbon disulfide, in which it is readily

soluble, and allowing the solution to evaporate slowly. The sulfur is deposited in octahedral-like crystals which have a density of 2.07,<sup>1</sup> and melt to a clear yellow liquid at  $113^{\circ}$ . If the clear crystals are kept for some time at temperatures between  $100^{\circ}$  and the melting-point they gradually become opaque and brittle, and when this change is complete, will melt at  $120^{\circ}$  instead of  $113^{\circ}$ , and have a density of 1.96 instead of 2.07. They then have undergone a transformation into  $\beta$  or



SULFUR

FIG. 30.

monoclinic sulfur (Fig. 30). This change is hastened by scratching the rhombic crystals with some hard point or by simply touching them with a monoclinic crystal.

Well defined crystals of monoclinic sulfur are easily obtained by melting some sulfur and allowing it to cool until a crust has formed on top. A hole is then made through this, and the still molten sulfur is poured out. The sides and bottom of the vessel will then be found covered with long needle-shaped monoclinic crystals. When first formed the crystals are amber colored, and may be bent slightly without breaking. If the crystals are kept at  $100^{\circ}$  or above, they retain their properties indefinitely, but if kept at ordinary temperatures for a day or so they change color to the lemon yellow of ordinary sulfur, become opaque, and increase in density to 2.07, in short they change into  $\alpha$  or rhombic sulfur. This transformation is hastened by contact with rhombic crystals. The external form of the crystals is that of the monoclinic, while internally they consist of an aggregation of rhombic crystals. Such crystals as these, which are internally of one form and externally of another, are called pseudomorphs.

**Transition Point.**—The facts just given indicate that the monoclinic form is stable at higher temperatures while the rhombic is at lower. There must be then a temperature at which they are both stable. This temperature is  $96^{\circ}$  and is called the transition point of these modifications of sulfur. From  $96^{\circ}$  to  $120^{\circ}$  the monoclinic modification is stable while the rhombic is stable below  $96^{\circ}$ .

At  $96^{\circ}$  the two modifications are in equilibrium, and hence have the same vapor pressure, solubility, etc. The monoclinic can exist below  $96^{\circ}$ , but in an unstable state and under these conditions it is more soluble than the rhombic and has a higher vapor pressure. Correspondingly, above  $96^{\circ}$  the rhombic is the unstable form and has the greater solubility and vapor pressure. These are simply examples of the general rule that the less stable modification has the higher solubility and vapor pressure.

Although unstable, the monoclinic sulfur can exist for a time below  $96^{\circ}$  and the rhombic above this temperature. This is due to what is called suspended transformation and is much the same phenomenon as the supercooling or superheating of water.

**Liquid Sulfur.**—Monoclinic sulfur melts at  $120^{\circ}$  to a light ellow, mobile liquid, which on cooling passes back into monoclinic crystals. If, however, the temperature be raised to  $160^{\circ}$  the liquid suddenly becomes dark in color and so viscous that the vessel may be inverted without the contents running out. At  $80^{\circ}$  the maximum viscosity is reached; at  $260^{\circ}$  the viscosity begins to decrease noticeably, and at  $444.6^{\circ}$ , the boiling-point of sulfur, the liquid is mobile once more.

The cause of this remarkable change at  $160^{\circ}$  is the appearance of a new form of liquid sulfur called  $\mu$  sulfur. When the dark colored liquid is slowly cooled the reverse change takes place, and the light yellow form reappears.

**Amorphous Sulfur.**—By heating sulfur to temperatures near its boiling-point and suddenly cooling the mass by pouring it in a thin stream into water, a clear, transparent, plastic, semi-fluid substance is obtained, which is called plastic sulfur. After a few days it becomes hard and opaque and is then found to consist of a mixture of rhombic crystals, soluble in carbon disulfide, and another form of sulfur which is insoluble in carbon disulfide. It is not crystalline and hence is called amorphous sulfur. It is supercooled sulfur, and changes slowly into the crystalline variety. The change takes years for completion at ordinary temperatures, but is finished in an hour at  $100^{\circ}$ .

There is another amorphous modification, soluble in carbon disulfide, and also soluble in water.

**Molecular Weight.**—At  $444.6^{\circ}$  sulfur boils. The vapor has an orange yellow color when just above its boiling-point. At  $500^{\circ}$  it is a deep red and then becomes lighter until at  $650^{\circ}$  it is a light yellow. The molecular weight at temperatures near the boiling-point is 230 and gradually falls until at  $1,000^{\circ}$  it reaches 64 and remains constant at this figure as the temperature is raised. Since the atomic weight of sulfur is a trifle over 32, the molecular weight of 230 corresponds to a formula of something between  $S_7$  and  $S_8$ , while that of 64 indicates a formula of  $S_2$ . The molecular weight of the element in solution as determined from the lowering of the freezing-point shows that when dissolved it has the formula  $S_8$ .

**Chemical Properties of Sulfur.**—Most all metals when finely powdered and rubbed in a mortar with sulfur combine directly

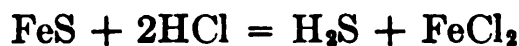
with the latter to form sulfides. At higher temperatures, the combination takes place so rapidly and with the evolution of so much heat that the general phenomena of combustion, the production of light, etc., are exhibited. The element will also unite with many of the non-metals; the halogens, hydrogen and oxygen for example.

With oxygen it forms the two very important compounds sulfur dioxide,  $\text{SO}_2$ , and sulfur trioxide,  $\text{SO}_3$ ; these are the anhydrides of sulfurous and sulfuric acids respectively. With hydrogen it forms the important compound hydrogen sulfide,  $\text{H}_2\text{S}$ .

**Uses of Sulfur.**—Thousands of tons of sulfur are used in the manufacture of sulfur dioxide which in turn is used for making sulfuric acid, in bleaching straw, wool, feathers, etc., and as a germicide. Sulfur is also employed in making carbon disulfide, gunpowder, matches, fireworks, sprays for fruit trees, and vulcanized rubber.

**Hydrogen Sulfide.**—Hydrogen sulfide is a gaseous substance whose formula is  $\text{H}_2\text{S}$ . It occurs in nature in the gases of some volcanoes, and is found in many mineral waters, which are commonly called sulfur waters. It may be prepared by the direct union of the elements by passing a stream of hydrogen through boiling sulfur. The reaction is reversible and hence is not complete.

Hydrogen sulfide is usually prepared by acting upon a sulfide, generally ferrous sulfide,  $\text{FeS}$ , with either dilute sulfuric or hydrochloric acid. The equation is



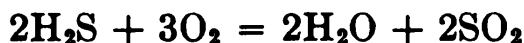
The ferrous sulfide is not very soluble in water but what does dissolve is largely broken up into ferrous and sulfur ions. Upon the addition of the acid, the sulfur ion unites with the hydrogen to form the very slightly dissociated compound hydrogen sulfide,  $\text{H}_2\text{S}$ . The water soon becomes saturated with this and then the substance is evolved in the gaseous state. The conditions are especially favorable for reaction in this case because we have a substance formed which is both slightly dissociated, and only moderately soluble. As fast as the sulfur ions present in solution are used up, more ferrous sulfide dissolves to keep up the supply. So the process continues until either the ferrous sulfide or the acid is consumed.

Hydrogen sulfide is also formed during the decay of albuminous substances such as eggs, etc. The odor of such substances in this condition is partly due to its presence.

**Physical Properties.**—Hydrogen sulfide is at ordinary temperatures a colorless, gaseous substance whose molecular weight 34.09. Its critical temperature is  $100^{\circ}$ , so it can be liquefied by pressure alone at ordinary temperatures. The critical pressure is 90 atmospheres. It boils at  $-61^{\circ}$  and freezes at  $-83^{\circ}$ . The liquid is chemically inactive. Hydrogen sulfide has a very disagreeable odor much like that of rotten eggs, and acts as a powerful narcotic poison when inhaled. Very dilute chlorine gas is used as an antidote.

Hydrogen sulfide is somewhat soluble in water. One volume of water dissolves 4.37 volumes at  $0^{\circ}$  and 3.23 at  $15^{\circ}$ . The solubility follows Henry's law *that the volume of a given gas dissolved by a fixed mass of a solvent is independent of the pressure, while the mass of the gas dissolved is directly proportional to the pressure.*

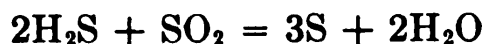
**Chemical Properties.**—Hydrogen sulfide burns in air with a pale blue flame, forming water and sulfur dioxide,  $\text{SO}_2$ ,



The equation shows that two volumes of  $\text{H}_2\text{S}$  require three volumes of oxygen for complete combustion. When mixed in these proportions the two gases explode violently upon the passage of an electric spark.

When the hydrogen sulfide is burned with an insufficient supply of air, water and free sulfur are the main products. This fact is taken advantage of for the recovery of sulfur from certain classes of waste products which will easily yield hydrogen sulfide.

With sulfur dioxide, hydrogen sulfide rapidly reacts, forming sulfur and water,

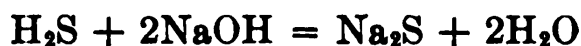


This is probably one of the reactions which gives rise to the volcanic sulfur.

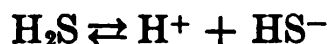
When heated to  $300^{\circ}$  it is slightly decomposed into hydrogen and sulfur, and at a white heat the decomposition is practically complete. At each temperature, there is a certain mixture of

hydrogen, sulfur, and hydrogen sulfide, at which equilibrium results.

**Solution in Water.**—A solution of hydrogen sulfide in water acts slightly acid toward litmus, and hence is sometimes called hydrosulfuric acid. Hydrogen sulfide is a very weak acid, and is but slightly dissociated. It differs from the acids which we have discussed in detail, except hydrofluoric, in that the two atomic weights of hydrogen per mole of hydrogen sulfide are both replaceable by metals and hence are ionizable. This state of affairs is described by the term dibasic, which means that one mole of the acids contains two atomic weights of replaceable hydrogen, and will react with two moles of a base like sodium hydroxide,



**Dissociation of Dibasic Acids.**—Hydrogen sulfide like all other dibasic acids, shows a marked tendency to ionize in such a way that only one hydrogen per mole is split off, as shown by the following equation,



This ionization is especially prominent in concentrated solutions. As the solution is diluted, or still better as the concentration of the hydrogen ion is reduced by neutralization with a base, the hydrosulfide ion,  $\text{HS}^-$ , breaks up into hydrogen and sulfur as ions,



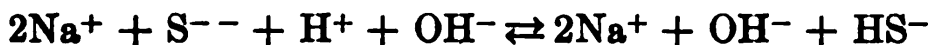
As a result of this tendency of dibasic acids, it is possible to obtain two series of salts of these acids according as the one or both hydrogen ions are replaced by metals. For example, we have the compounds  $\text{NaHS}$  and  $\text{Na}_2\text{S}$ . The compound  $\text{NaHS}$  is often called sodium hydrosulfide from its resemblance to sodium hydroxide,  $\text{NaOH}$ , while  $\text{Na}_2\text{S}$  is called sodium sulfide. Several other names for the same compounds are in common use as shown by the following table:

$\text{NaHS}$	$\text{Na}_2\text{S}$
Acid sodium sulfide	Neutral sodium sulfide
Primary sodium sulfide	Secondary sodium sulfide
Mono-sodium sulfide	Di-sodium sulfide

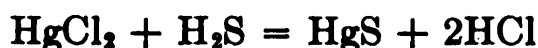
The terms acid and neutral sodium sulfide are rather deceptive, since the so-called acid salt is really just about neutral in its action upon litmus, while the neutral salt is decidedly alkaline. This latter effect is due to hydrolysis which changes the neutral sulfide nearly completely to the acid sulfide according to the equation,



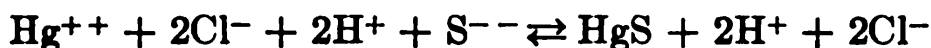
or



**Analytical Reactions of Hydrogen Sulfide.**—The sulfides of many of the metals are very slightly soluble in water and are consequently precipitated when hydrogen sulfide is passed into aqueous solutions of their salts. For example, a solution of mercuric chloride,  $\text{HgCl}_2$ , gives a black precipitate of mercuric sulfide,  $\text{HgS}$ , with hydrogen sulfide,

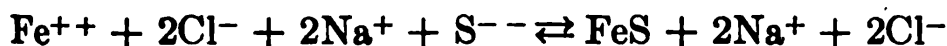


or



Salts of copper, lead, bismuth, antimony, tin, and several other metals act in the same way, and their sulfides are so difficultly soluble that they will be formed even in fairly acid solutions.

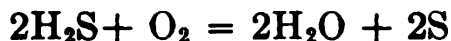
Other sulfides are more soluble, and require a higher concentration of sulfur as ion for their formation. This can be obtained by taking advantage of the fact that salts of weak acids are highly dissociated, and using instead of hydrogen sulfide, sodium or ammonium sulfide. For example, ferrous sulfide is not precipitated by hydrogen sulfide, but is by sodium sulfide,



Use is made of these properties of the sulfides to separate the metals into groups according to similarities in their behavior, and this together with the fact that many of the sulfides have distinctive colors, makes hydrogen sulfide an exceedingly important reagent.

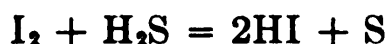
**Hydrogen Sulfide as a Reducing Agent.**—An aqueous solution of hydrogen sulfide when exposed to the air loses its odor and becomes milky, finally depositing a white precipitate of finely

divided sulfur. This is formed by the oxidation of the hydrogen sulfide by the oxygen of the air,

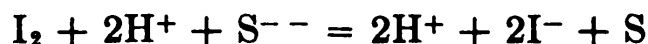


The oxygen oxidizes the hydrogen sulfide, and the latter reduces the oxygen.

When hydrogen sulfide is passed into water in which iodine is present a solution of hydriodic acid is obtained together with free sulfur,

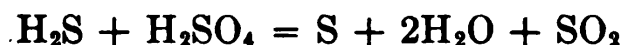


or expressed as ions,



In this case the action is easily seen to be between the sulfur ion and the thing reduced—the iodine. Upon examination of the other cases in which hydrogen sulfide acts as a reducing agent, it will be found that in the majority of cases the action consists in the transformation of the sulfur ion into free sulfur, but sometimes sulfuric acid is formed. The hydrogen has nothing to do with the reducing action.

Hydrogen sulfide will reduce concentrated sulfuric acid to water and sulfur dioxide, sulfur being set free,



Because of this action, concentrated sulfuric acid cannot be used to dry hydrogen sulfide.

**Polysulfides.**—When a solution of a soluble sulfide or acid sulfide is brought in contact with sulfur, the latter is dissolved and the solution becomes dark yellow in color. If sodium sulfide is used, compounds  $\text{Na}_2\text{S}_4$ , and  $\text{Na}_2\text{S}_5$  may be obtained. These substances are called polysulfides. They are salts and yield ions which are  $\text{Na}^+$  and anions which vary in composition from  $\text{S}_4^{--}$  or  $\text{HS}_4^-$  to  $\text{S}_5^{--}$  or  $\text{HS}_5^-$ .

**Sulfur Dioxide or Sulfurous Anhydride.**—Sulfur dioxide, at ordinary temperatures, is a gaseous substance which is present in the gases given off by many volcanoes. It is formed, as we have seen, by burning sulfur or hydrogen sulfide in the air. It may also be prepared by roasting metallic sulfides, pyrite,  $\text{FeS}_2$ ,

for example, in the air. When these are raised to the required temperature they burn, forming sulfur dioxide,  $\text{SO}_2$ , and the oxides of the metals,



Many of the metals are obtained from their sulfides and such a roasting process is generally a necessary preliminary to the reduction to the metal.

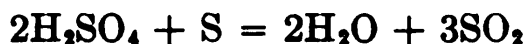
Sulfur dioxide may be very conveniently prepared by the action of acids upon sulfites or acid sulfites. Under these conditions we should expect the formation of sulfurous acid,  $\text{H}_2\text{SO}_3$ , and this is doubtless formed first but breaks down into water and  $\text{SO}_2$ . The most convenient laboratory method for its preparation is based upon this, sodium acid sulfite,  $\text{NaHSO}_3$ , and strong sulfuric acid being used:



It is often prepared by the action of reducing agents upon concentrated sulfuric acid. The most suitable ones are perhaps metallic copper or free sulfur, the equations being:



or



A good deal of sulfur dioxide is prepared for technical purposes by acting upon concentrated sulfuric acid with carbon,



The presence of the carbon dioxide mixed with the sulfur dioxide usually makes this method unsuitable for laboratory purposes. The greater part of the sulfur dioxide which is used in the arts is made by burning sulfur or pyrite.

**Physical Properties.**—Sulfur dioxide is a colorless gaseous substance with a strong odor which is familiar as the odor of burning sulfur. Its critical temperature is  $156^\circ$  and the critical pressure is 79 atmospheres. It may, then, be liquefied by pressure alone at ordinary temperatures. Since its boiling-point is  $-10^\circ$ , it may be easily liquefied by a mixture of ice and salt. The liquid

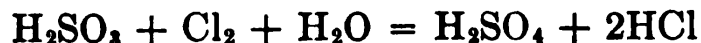
is as clear and colorless as water. It is a fairly good solvent and is able to ionize many salts, though to a smaller extent than water. Liquid sulfur dioxide is now an article of commerce, being sold in metal cylinders from which it may be removed as desired.

At ordinary temperatures sulfur dioxide deviates widely from the gas laws—a fact which is connected with its ease of liquefaction. It is rather soluble in water, one volume of the latter taking up at ordinary temperatures 50 volumes of sulfur dioxide and a smaller quantity at higher temperatures. At higher temperatures the solubility approximately follows Henry's law. The aqueous solution smells strongly of the dioxide which can be completely removed by boiling since it does not form either a maximum or minimum boiling mixture with water.

**Chemical Properties.**—Sulfur dioxide is stable and is decomposed only at very high temperatures. It will unite directly with chlorine for the formation of sulfuryl chloride,  $\text{SO}_2\text{Cl}_2$ , or with oxygen to form sulfur trioxide,  $\text{SO}_3$ . The solution of sulfur dioxide in water reacts acid and when neutralized with sodium hydroxide and the solution evaporated, it yields the salt, sodium sulfite,  $\text{Na}_2\text{SO}_3$ . We therefore say that the solution contains **sulfurous acid**, and ascribe to this the formula  $\text{H}_2\text{SO}_3$ . A pure acid of this composition cannot be prepared since it breaks down into water and sulfur dioxide as the solution is concentrated. Because of the formation of sulfurous acid, sulfur dioxide is often called sulfurous anhydride.

Like hydrogen sulfide, sulfurous acid is a dibasic acid and yields acid and normal salts. It is a stronger acid than hydrogen sulfide, and the normal salts are not so highly hydrolyzed as the normal sulfides. The hydrolysis, however, is marked.

**Reducing Action.**—Sulfurous acid and the sulfites are strong reducing agents, passing into sulfuric acid or sulfates. As an example, we may take the reaction of sulfurous acid upon chlorine and water,



Here the oxygen necessary for the formation of sulfuric acid comes from the water. The sulfurous acid may be replaced by sulfites.

Because of this reaction between chlorine and sulfurous acid,

sulfurous acid and sulfites are used as "antichlors" in the bleaching industries to remove the last of the chlorine.

Sulfites are spontaneously oxidized by the oxygen of the air, an action which may be greatly slowed down by the addition of small quantities of sugar, alcohol, or glycerine, which act as negative catalyzers.

**Bleaching Action.**—Sulfurous acid and its salts are rather powerful bleaching agents and are extensively used for bleaching silk, wool, feathers, straw, etc., which would be destroyed by chlorine or hypochlorous acid. The sulfurous acid acts very differently from the chlorine in that it reduces the coloring matter instead of oxidizing it. The coloring matters are not destroyed in this case and after the process is finished the goods must be carefully washed to remove the altered coloring matter, as otherwise the oxygen of the air would soon restore the color. If sulfur dioxide is used, the goods are first moistened so that sulfurous acid may be formed.

**Action on Organisms.**—Sulfur dioxide, sulfurous acid and sulfites are powerful poisons toward vegetable organisms of all kinds. Because of this property, sulfur dioxide is used as a germicide and fungicide. Sulfurous acid and sulfites have been much used as preservatives in food products, but are now generally forbidden.

**Sulfur Trioxide or Sulfuric Anhydride.**—Sulfur trioxide is formed by the direct union of sulfur dioxide and oxygen,



The action, however, takes place very slowly even at somewhat elevated temperatures. In this case, one cannot resort to raising the temperature to a very high point in order to increase the rate of combination, because of the fact that at a high temperature the action is reversed. However, there are several substances, notably finely divided platinum and ferric oxide,  $\text{Fe}_2\text{O}_3$ , which will actively catalyze the union of the gases. In the case of the finely divided platinum, the process takes place to the best advantage when the temperature is about  $400^\circ$ . The sulfur trioxide so formed may be condensed to a colorless mobile liquid which boils at  $46^\circ$ . When cooled, it forms a transparent glassy solid which melts at  $15^\circ$ . After standing for some time,

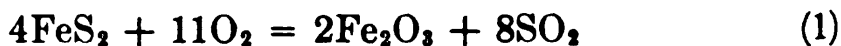
it passes over into a more stable form which appears as a white, opaque, glistening mass of needle-shaped crystals. This opaque form does not melt, but at 50° passes directly into the vapor which upon being cooled condenses to the liquid, from which the ice-like solid may first be obtained and then finally the opaque form. The white, crystalline solid has the formula  $S_2O_6$ , while that of the other modification is  $SO_3$ . The  $S_2O_6$  is called a polymer of the  $SO_3$ . The formation of the liquid and glassy solid before the appearance of the stable opaque form is another instance of the phenomena described by the law of successive reactions.

**Action on Water.**—When sulfur trioxide comes in contact with moist air, it forms dense white fumes, consisting of sulfuric acid formed by the union of the sulfur trioxide with water vapor. When the trioxide is brought in contact with water, combination takes place with the production of so much heat that it hisses as though a red hot body were plunged into the water. The result of this action is sulfuric acid, so sulfur trioxide is often called sulfuric anhydride.

Sulfuric acid is an exceedingly important chemical as may be seen from its yearly production which amounts to over 2,000,000 tons in this country alone. It is made by two processes. The first, called the contact process, is very simple in theory, but has certain practical difficulties, and is best adapted to the production of very concentrated acid.

The second is the lead chamber process, the chemistry of which is more complex but whose operation is sure and simple. This turns out immense quantities at a low cost of a somewhat dilute acid suitable for many purposes, the bulk of it being used for preparing phosphate fertilizer.

The starting-point in each process is the preparation of sulfur dioxide either by burning sulfur in the air or more commonly by roasting a sulfide such as pyrite,  $FeS_2$ ; in the latter case the reaction is,



In each process with the aid of catalyzers this sulfur dioxide, oxygen of the air and water are then caused to react for the formation of sulfuric acid. The chemistry of the **contact process**

s very simple. Three reactions in addition to that in equation (1) are involved: First the formation of sulfur trioxide,



Second, the union of the sulfur trioxide with sulfuric acid to form fuming or pyrosulfuric acid,  $\text{H}_2\text{S}_2\text{O}_7$



Third, the dilution of this fuming acid with just enough water to make the product 100 per cent. sulfuric acid



The reaction between sulfur dioxide and oxygen (2) is the troublesome one. It is slow, reversible, and far from complete at temperatures above  $400^\circ$ . Because of its slowness a positive catalyzer, either platinum or ferric oxide, must be used. Platinum works rapidly at  $400^\circ$ , and at this temperature 98–99 per cent. of the  $\text{SO}_2$  may be oxidized to trioxide.

But the platinum is quickly “poisoned” by the small quantities of arsenic compounds present in the dust from the sulfur or

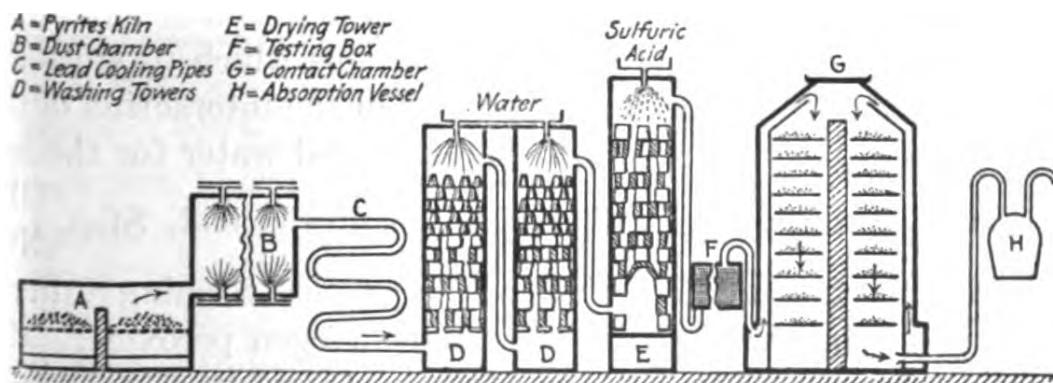


FIG. 31.

pyrite burners, and soon loses its activity as a catalyzer unless the sulfur dioxide is purified with painful care by first allowing the dust to settle (Fig. 31), then cooling the gas, washing it with a spray of water and drying with sulfuric acid before it goes to the catalyzer in the contact chamber. Ferric oxide is not poisoned by arsenic but works rapidly enough only at temperatures of  $625^\circ$  or higher, and at  $625^\circ$  not more than 70 per cent. of the dioxide can be converted into trioxide. Hence ferric oxide is much less efficient than the more expensive

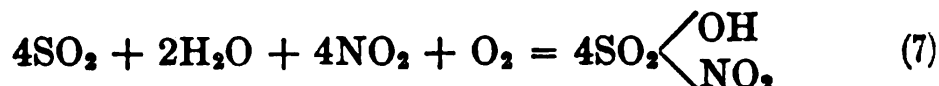
and troublesome platinum, so platinum is the catalyzer most commonly used. The plant is shown diagrammatically in Fig. 31. The reaction represented by equation (1) takes place in A; by equation (2), in G; and (3), in H; where the sulfur trioxide, removed from the nitrogen and oxygen left from the air by absorption in concentrated sulfuric acid, forms fuming sulfuric acid, which upon dilution gives sulfuric acid as shown in (4).

**Lead Chamber Process.**—In this very important process, nitrogen peroxide,  $\text{NO}_2$ , catalyzes the formation of sulfuric acid from the sulfur dioxide, oxygen and water.

The sulfur dioxide is prepared as before, see equation (1). The oxygen comes from the air. The nitrogen peroxide,  $\text{NO}_2$ , comes from the action of sulfur dioxide and water upon nitric acid, giving sulfuric acid and nitric oxide,  $\text{NO}$ ; the latter then reacts with the oxygen of the air to form nitrogen peroxide. The equations are as follows:



The water is introduced either in the form of steam or as a spray of very finely divided water. The reactions which produce the greater part of the sulfuric acid consist in the interaction of the sulfur dioxide, oxygen, nitrogen peroxide and water for the formation of a compound called nitrosylsulfuric acid,  $\text{SO}_2 \begin{smallmatrix} \text{OH} \\ \diagup \\ \text{NO}_2 \end{smallmatrix}$ , and its subsequent decomposition by water, forming sulfuric acid and a mixture of nitric oxide and nitrogen peroxide. The equations are



and



The nitric oxide then reacts with some more oxygen as shown in equation (6) to reform the peroxide which will at once react with more of the sulfur dioxide, oxygen, and water to form more nitrosylsulfuric acid, which is decomposed by water, forming another lot of sulfuric acid and reproducing the oxides of nitrogen.

This cycle of changes goes on until all but one-half a per cent. of the sulfur dioxide is used up. So a very small quantity of the oxides of nitrogen will transform a large amount of sulfur dioxide. These reactions take place in very large lead lined rooms or chambers (Fig. 32), of which there are three or more in each plant. These chambers are often 100 ft. or more in length and hold from 150,000 to 200,000 cu. ft. Lead is used in their construction because it is but little attacked by dilute sulfuric acid. The sulfuric acid formed collects on the bottom of the

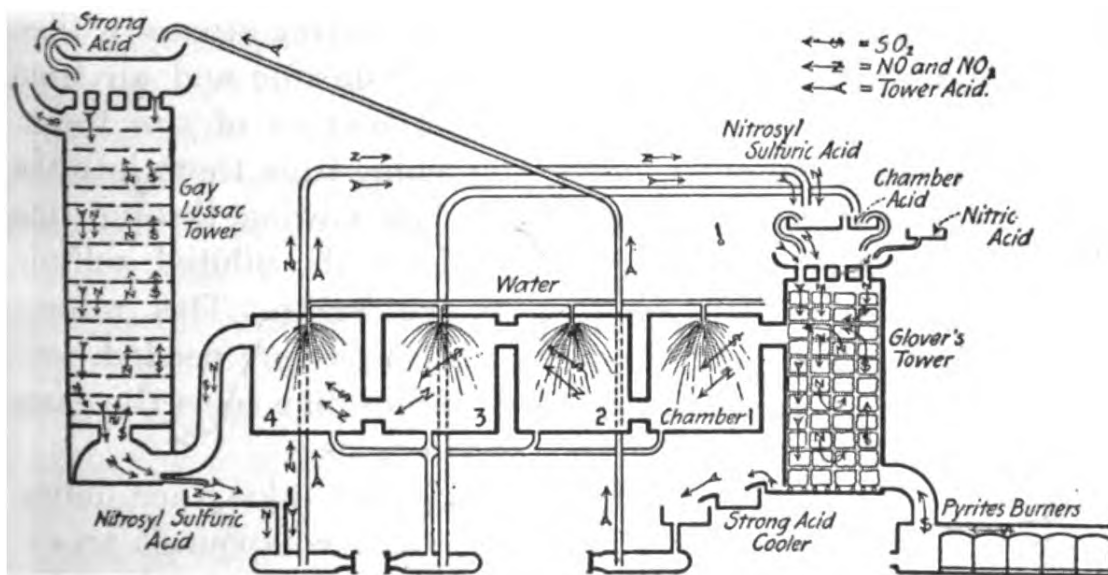
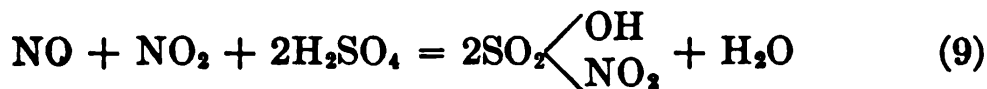


FIG. 32.

chambers, while a mixture of the oxides of nitrogen and the nitrogen from the air which furnished the oxygen issues from the last chamber. The oxides of nitrogen are too valuable to be lost so advantage is taken of the fact that they may be absorbed in concentrated sulfuric acid forming nitrosylsulfuric acid,



This, it will be noticed, is equation (8) written reversed. The absorption takes place in what is called the Gay Lussac tower. This is about 50 ft. high and is filled with tiles over which concentrated sulfuric acid runs in a thin stream, while the gases from the last lead chamber enter at the bottom and leave near the top. The acid, which collects at the bottom of the tower, contains the nitrosylsulfuric acid in solution. This may be

easily decomposed by water, regenerating the oxides of nitrogen necessary for catalyzing the formation of the sulfuric acid. But to be of service, these oxides of nitrogen must be reintroduced into the first lead chamber. This is done by elevating the acid drawn off from the bottom of the Gay Lussac tower, with compressed air to the top of a similar structure called the Glover's tower which just precedes the first lead chamber. Here the concentrated sulfuric acid is mixed with dilute acid from the chambers. This partly decomposes the nitrosylsulfuric acid. (See equation 8). The mixture is then allowed to flow slowly down through the tower over the acid-resisting stones or tiles. On its way down it meets the hot sulfur dioxide and air from the burners. These gases enter at the bottom of the tower, pass up through and out near the top, going from there into the first lead chamber. The hot gases while flowing through the tower remove the oxides of nitrogen from the diluted sulfuric acid and evaporate a large part of the water. This returns the oxides of nitrogen to the point where they are needed, concentrates the sulfuric acid, and at the same time cools the gases to the temperature favorable for the reactions.

Other reactions than the ones given above take place during the process, whereby a part of the nitrogen compounds are reduced to nitrous oxide,  $N_2O$ , and, as this takes no further part in the reaction, it constitutes a loss of active nitrogen to the system. To make up for this and for mechanical losses, it is necessary to use about 4 parts of sodium nitrate for every 100 parts of sulfur burned, to make nitric acid enough to replace the oxides of nitrogen lost. The nitric acid is usually added at the top of the Glover's tower and here reacts with the sulfur dioxide as shown in equation (5).

The whole process may be briefly summed up as follows: Sulfur dioxide is formed in the pyrite burner, equation (1). The hot gas passes either directly to the Glover's tower or sometimes first through a dust-settling chamber. In the Glover's tower the oxides of nitrogen are removed from the nitrosylsulfuric acid, equation (8), losses replaced by the addition of nitric acid, equation (5), and part of the chamber acid concentrated. In addition, reactions represented by equations (6), (7), and (8) take place to a certain extent in the tower. From

the Glover's tower, the gases pass on through the lead chambers in which the principal reactions are represented by equations (6), (7), and (8). From the last chamber, the residual gases pass through the Gay Lussac tower where the oxides of nitrogen dissolve in concentrated sulfuric acid, forming nitrosylsulfuric acid as shown in equation (9). The nitrosylsulfuric acid then goes back to the Glover's tower and the oxides of nitrogen begin their journey once more.

**Concentration of the Acid.**—The chamber acid from the sulfuric acid plant runs about 65 per cent. acid and 35 per cent. water. Enormous quantities of it are used at this strength, for example, in making fertilizer, but for many purposes the greater part of the water must be removed. This is very commonly done by running the chamber acid together with that from the Gay Lussac tower through the Glover towers until the acid has reached a concentration of 78 per cent. or higher. It may then be concentrated still further by heating in cast-iron retorts, because sulfuric acid of this strength or stronger does not attack iron, while the weaker acid does. An entirely adequate explanation of this behavior is lacking.

Stills of glass or of platinum lined with gold are sometimes used instead of the cast-iron ones.

Another method of concentration which is sometimes used is to evaporate the chamber acid in lead pans heated from above until the acid has a density of 1.71 corresponding to 73 per cent. acid, when it becomes a strong enough oxidizing agent to attack the lead rapidly. Further concentration must then be done in cast-iron, glass, or platinum.

**Physical Properties.**—Commercial sulfuric acid or oil of vitriol has a density of 1.83–1.84 and contains 94 per cent. of the acid. The strongest sulfuric acid which can be secured by evaporation has a density of 1.841 and contains 98.2 per cent. of the acid. This is the composition of the maximum boiling mixture. It boils at 330° C. The vapor consists largely of a mixture of sulfur trioxide and water as may be demonstrated by the fact that a flask filled with sulfuric acid vapor will lose water more rapidly by diffusion than it does the more dense sulfur trioxide. When concentrated sulfuric acid is cooled to a low temperature, crystals of the pure acid,  $\text{H}_2\text{SO}_4$ , separate. These melt at 10.5°.

**Aqueous Sulfuric Acid.**—The heat of solution of one mole of sulfuric acid in a great deal of water is 75 Kj. So when sulfuric acid is mixed with water a great amount of heat is evolved. The acid should always be poured into the water, as otherwise so much heat is likely to be developed at one point that some of the water will be suddenly converted into steam, causing the sulfuric acid to spatter.

When concentrated sulfuric acid is mixed with water considerable contraction occurs so that the total volume is less than the sum of the volumes of the water and the acid. The greatest contraction takes place when the diluted acid has a composition of 70 per cent. A total volume of 100 c.c. before the mixing becomes about 97 after the solution of the acid and cooling.

The vapor pressure of water from aqueous solutions of the acid varies continuously with the composition, and is very small indeed at ordinary temperatures from the more concentrated acid. Upon this fact depends the usefulness of concentrated sulfuric acid for drying gases.

**Dissociation of Sulfuric Acid.**—Pure concentrated sulfuric acid is not a good conductor of electricity, but when the acid is dissolved in water it becomes a very good conductor indeed. It is a dibasic acid, and like all others of its class, dissociates in two ways. In the more concentrated acid, the principal anion is  $\text{HSO}_4^-$ , but as the acid is diluted this breaks down to give  $\text{H}^+$  and  $\text{SO}_4^{--}$ . As has been pointed out, it is a strong acid but not so strong as hydrochloric.

**Applications of Sulfuric Acid.**—Enormous quantities of sulfuric acid are used in the arts. The largest single use is in the manufacture of fertilizers. A great deal is used in making sodium carbonate. In fact, there is scarcely a manufacturing industry of any importance which does not directly or indirectly make use of sulfuric acid.

Its many applications depend mainly upon the following facts. It is cheap, a fairly strong acid, a moderately strong oxidizing agent, not very volatile and forms slightly soluble salts with several cations. As an acid it is much used, for example, in the preparation of hydrogen, to dissolve the "scale" or coating of oxide from metal plates before further treatment in various manu-

cturing processes and in the preparation of other acids from air salts.

Advantage is taken of its oxidizing power in the separation of silver from gold in the process of refining of these metals. The silver is oxidized to silver as ion, which then forms silver sulfate, while the sulfuric acid is reduced to water and sulfur dioxide. The gold is not attacked.



Its extensive use in the manufacture of hydrochloric and other acids by the first general method depends upon its slight volatility, which more than makes up for the fact that sulfuric acid is weaker than many of the acids which it is used to prepare. The slight solubility of the sulfates of barium, lead, and calcium makes it very useful in the preparation of acids by the second general method. In fact, its use in preparing fertilizers depends upon the fact that it can convert calcium phosphate into easily soluble phosphoric acid or else calcium acid phosphate and difficultly soluble calcium sulfate.

**Sulfates.**—Since sulfuric acid is a dibasic acid, it forms two series of salts, acid and neutral sulfates; for example, sodium acid sulfate  $\text{NaHSO}_4$  and sodium neutral sulfate  $\text{Na}_2\text{SO}_4$ . Sulfuric acid is a strong enough acid to make the names appropriate because the acid salt actually is acid and the neutral salt, neutral. The various sulfates will be discussed in some detail under the different metals.

**Identification.**—Barium sulfate is exceedingly slightly soluble in water, since it requires more than 300,000 times its weight of water for solution. It is promptly formed whenever a solution of a barium salt, barium chloride,  $\text{BaCl}_2$ , for example, is added to a solution of a sulfate or of sulfuric acid. This then is a property of the sulfate ion. The barium sulfate is white, and is not dissolved in dilute hydrochloric acid, and by this is distinguished from all other barium salts, except barium selenate.

#### OTHER OXYGEN ACIDS OF SULFUR

**Persulfuric Acid.**—It will be recalled that when dilute sulfuric acid is electrolyzed, hydrogen and oxygen are given off in the proportion for the formation of water.

When 50 per cent. sulfuric acid is electrolyzed, using a very small anode and keeping the solution cold, but little oxygen appears at the anode. At the same time a new substance, persulfuric acid,  $\text{H}_2\text{S}_2\text{O}_8$ , is formed in the solution. The formation of this acid is easily understood. Sulfuric acid as concentrated as 50 per cent. or more contains principally the ions  $\text{H}^+$  and  $\text{HSO}_4^-$ . Two ionic weights of  $\text{HSO}_4^-$  give up their charge to the anode and at once unite to form  $\text{H}_2\text{S}_2\text{O}_8$ . If potassium or ammonium acid sulfate,  $\text{KHSO}_4$  or  $\text{NH}_4\text{HSO}_4$ , is used instead of the sulfuric acid, the rather difficultly soluble potassium or ammonium persulfate soon separates around the anode. These salts are now common commercial articles, and find fairly extensive use because they are good oxidizing agents.

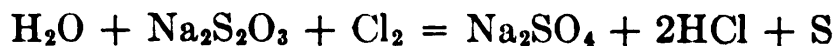
**Hyposulfurous Acid.**—The salts of this acid  $\text{H}_2\text{S}_2\text{O}_4$  are formed by the action of zinc upon solutions of acid sulfites containing an excess of sulfur dioxide, or upon sulfur dioxide in solution in absolute alcohol. Sodium hyposulfite,  $\text{Na}_2\text{S}_2\text{O}_4$ , is a commercial article which is extensively used in dyeing.

The hyposulfites are less powerful reducing agents than zinc, but being soluble are much more rapid in their action.

**Thiosulfuric Acid.**—It will be recalled that a sulfite in solution will slowly take up oxygen from the air, passing into a sulfate. In much the same way, but more rapidly, a sulfite, say sodium sulfite, will take up sulfur forming a thiosulfate, or a sulfate in which one atomic weight of sulfur takes the place of an atomic weight of oxygen. This is one of the ways in which sulfur shows its analogy to oxygen,



The salt  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  is known as sodium thiosulfate or incorrectly as sodium hyposulfite or "hypo." It is the most important of the thiosulfates and is much used in photography. It is a good reducing agent and is often used as such in place of sulfites. For example, it may be used as an antichlor for the removal of chlorine from bleached goods,



The protective masks worn by the soldiers in the European war to minimize the effect of the "asphyxiating gas," chlorine,

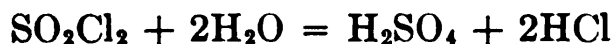
were wet with a solution of sodium thiosulfate and carbonate, the equation given above represents the main reaction.

Thiosulfuric acid is so unstable that it decomposes almost as soon as it is liberated, into sulfur and sulfurous acid. So that if a solution of thiosulfate is acidulated it will become milky almost at once. This decomposition is largely prevented by the addition of sulfites.

**Halogen Compounds of Sulfur.**—When dry chlorine gas is passed over heated sulfur, the two elements combine with the formation of sulfur monochloride  $S_2Cl_2$ , which is a reddish-yellow liquid boiling at  $138^\circ$ . It is a very good solvent for sulfur and for this reason has been used in vulcanizing rubber. With water, it reacts for the formation of sulfur, hydrochloric acid, sulfurous acid, and thiosulfurous acid.

With bromine and iodine, sulfur forms compounds corresponding to the monochloride. They are the monobromide,  $S_2Br_2$ , and the moniodide,  $S_2I_2$ . Fluorine and sulfur combine so vigorously that they catch fire at ordinary temperatures forming sulfur hexafluoride,  $SF_6$ .

**Sulfuryl Chloride.**—Sulfur dioxide and chlorine combine directly to form sulfuryl chloride,  $SO_2Cl_2$ . The combination takes place much more rapidly in the sunlight than in diffused daylight and is catalyzed by camphor. It is a colorless mobile liquid, boiling at  $69^\circ$ , and having a density of 1.67. With water it reacts to give sulfuric and hydrochloric acids,



**Positive and Negative Valence.**—Hydrogen and chlorine in hydrogen chloride as we have learned are both monovalent. When the compound is dissolved in water it dissociates into the monovalent hydrogen ion carrying one positive charge, and the monovalent chlorine ion carrying a negative charge. This at once gives the conception of positive and negative valence, and the explanation of the valence of an ion, which then becomes identical with the number of positive or negative charges which the ion carries. Thus the sulfur ion,  $S^{--}$ , is negative and is divalent, as is also the sulfate ion,  $SO_4^{--}$ . We may, then, say that the sulfate ion unites with two atomic weights of hydrogen or sodium as ion; because each of these carries one positive

charge or is monovalent, and two are required to neutralize the charge upon the sulfate ion and to form sulfuric acid or sodium sulfate, both of which are electrically neutral. The subject of the valence of ions is simple, and this has led to attempts to ascribe the phenomena connected with valence in general to an electrical origin. In accordance with this view, the elements, even in compounds, which are not salts, are supposed to be charged, some positively and some negatively and the valence of each element is supposed to be determined by the number of + or - charges which it carries per atomic weight. This view seems to be not entirely free from contradictions and may be incorrect, but it is in agreement with the facts in the great majority of cases and is a very useful conception. According to this hypothesis, the oxygen in water and most other compounds carries two, the nitrogen in ammonia three, and the carbon in methane,  $\text{CH}_4$ , four negative charges.

While it is very easy to decide that the valence of the sulfate ion is two, it is not so easy to answer the question "What is the valence of the sulfur in this ion?" If we assume that oxygen in compounds always has the valence that it has in water, viz., two negative, we may reach a reasonable conclusion in this and similar cases. Since the sulfate ion as a whole carries two negative charges, it follows that the algebraical sum of the positive and negative charges upon the sulfur and the oxygen must be  $-2$  or  $x + a = -2$ , where "x" represents the charges upon the sulfur, and "a" those upon the oxygen. Now from the assumption which we have made about the valence of oxygen, each atomic weight of this element carries two negative charges, and the four would then total eight negative charges, and in the equation given above, "a" would have the value  $-8$

$$x - 8 = -2$$

or

$$x = +6$$

From this it follows that the valence of the sulfur in the sulfate ion or in sulfuric acid for that matter, is  $+6$ . This is confirmed by the fact that sulfuric acid is so simply formed from water and sulfur trioxide  $\text{SO}_3$ , in which the sulfur evidently has a valence of  $+6$ . Working in this same way, it is easy to show that

the chlorine in chloric acid,  $\text{HClO}_3$ , has a valence of +5, in sodium chlorite,  $\text{NaClO}_2$ , of +3, and that the phosphorus in phosphoric acid,  $\text{H}_3\text{PO}_4$ , has a valence of +5. Nitrogen in ammonia  $\text{NH}_3$ , and in the ammonium ion  $\text{NH}_4^+$ , seems to have a valence of -3; while in nitric acid  $\text{HNO}_3$ , it is +5, so it would appear that the valence of an element can not only change in value but even in sign.

The valence of a free element is considered to be zero.

**Oxidation and Reduction.**—Oxidation and reduction processes have been frequently mentioned in what has gone before, but have not been discussed in detail. While oxygen is the typical oxidizing agent, attention has been called a number of times to the fact that we have well marked cases of oxidation into which oxygen does not enter in any way. Similarly hydrogen is the typical reducing agent, but a great many reduction processes are known which do not involve this element.

A study of these processes soon shows that they always produce changes in the valence of the elements oxidized or reduced. That this is so may be easily seen from the table given below.

An inspection of the last three columns in the first table will show that oxidation is always accompanied by an increase in the number of positive charges upon the element oxidized, a decrease in negative being of course equivalent to an increase in the positive charges. The corresponding columns of the second table indicate that reduction involves a decrease in the number of

TYPES OF CHANGES WHICH ARE CONSIDERED OXIDATION

Substance oxidised	Oxidising agent	Substance formed	Valence of the oxidised substances		Change in valence
			Before	After	
Mg	$\text{O}_2$	MgO	0	+2	+2
Zn	$\text{H}^+$	$\text{Zn}^{++}$	0	+2	+2
$\text{I}_2$	$\text{KClO}_3$	$\text{IO}_3^-$	0	+5	+5
$\text{Fe}^{++}$	$\text{Cl}_2$	$\text{Fe}^{+++}$	+2	+3	+1
$\text{Cl}^-$	$\text{MnO}_2$	$\text{Cl}_2$	-1	0	+1
$\text{S}^-$	$\text{I}_2$	S	-2	0	+2
$\text{S}^-$	$\text{Br}_2(\text{H}_2\text{O})$	$\text{SO}_4^{--}$	-2	+6	+8
$\text{SO}_3^{--}$	$\text{O}_2$	$\text{SO}_4^{--}$	+4 (of S)	+6 (of S)	+2

## TYPES OF CHANGES WHICH ARE CONSIDERED REDUCTION

Substance reduced	Reducing agent	Substance formed	Valence of the reduced substance		Change in valence
			Before	After	
$\text{Cu}^{++}$	Zn	Cu (metal)	+2	0	-2
$\text{Ag}^+$	$\text{H}_2$	Ag (metal)	+1	0	-1
$\text{I}_2$	$\text{S}^{--}$	$\text{I}^-$	0	-1	-1
$\text{NO}_3^-$	Cu	NO	+5 (N)	+2 (N)	-3
$\text{NO}_3^-$	Al (in KOH)	$\text{NH}_3$	+5	-3	-8
$\text{ClO}_3^-$	$\text{SO}_3^{--}$	$\text{Cl}^-$	+5	-1	-6
$\text{O}_2$	Mg	$\text{O}^{--}$	0	-2	-2

positive or an increase in the number of negative charges upon the element reduced. The most general conception of oxidation and reduction then is that *oxidation consists in an increase in the number of positive charges upon the element oxidized or what amounts to the same thing, a decrease in the number of negative charges. Reduction consists in a decrease in the number of positive charges upon the element reduced, or what amounts to the same thing, an increase in the number of negative charges.* Oxidation and reduction are opposed processes, and one of them cannot take place without the other occurring simultaneously and to the same extent. This will be seen by examining the above table more closely. In each of these reactions, there is an oxidizing agent and a reducing agent, and in every case the one loses exactly as many charges as the other gains.

## CHAPTER XIII

### SELENIUM AND TELLURIUM

Selenium and tellurium are two elements which bear about the same relation to sulfur that bromine and iodine do to chlorine. The resemblance of tellurium to sulphur is perhaps less marked than that of iodine to chlorine, but selenium furnished fully as close a match for sulfur as bromine does for chlorine. A comparison of the atomic weights of the members of these two groups of elements is of some interest.

Chlorine.....	35.46	Bromine.....	79.92	Iodine.....	126.92
Sulfur.....	32.06	Selenium.....	79.20	Tellurium.....	127.50

From this it is seen that the atomic weights of sulfur, selenium, and tellurium correspond closely to those of chlorine, bromine, and iodine respectively. In each group of these elements it becomes easier to liberate an element from its hydrogen compound, the greater the atomic weight of the element is. Selenium and tellurium correspond to bromine and iodine in that they do not occur abundantly in nature although they are rather widely distributed.

#### SELENIUM

Selenium occurs in nature both free and combined. In the free state it is found as an impurity in crystals of native sulfur, while the compounds are usually associated with the corresponding sulfur compounds. The element was discovered in the flue dust of a sulfuric acid factory, and this together with the anode mud of electrolytic lead and copper refineries is still the chief source of the element.

**Properties.**—Like sulfur, selenium takes on a number of forms; amorphous, crystalline and metallic. Amorphous selenium is black and glassy unless finely powdered when it is red. There are two kinds of red crystalline selenium; they melt at

170°–180° and are soluble in carbon disulfide. If kept at 150° for some time, they change into a gray crystalline modification melting at 217° and boiling at 690°. This gray form has some metallic properties and is a poor conductor of electricity in the dark, but much better in the light. This is the basis of the selenium cells which find practical application in automatically turning on signal lights at the approach of darkness. Above 1,400° the molecular weight corresponds to the formula  $\text{Se}_2$ ; at lower temperature the molecule is more complex.

**Chemical Properties.**—Selenium combines directly with iron and many other metals, and also with hydrogen, oxygen and the halogens. As a rule these compounds are formed less readily than the corresponding sulfur compounds, and from them the element is more easily liberated than is sulfur from its compounds. These relations are about the same as those between bromine and chlorine.

**Hydrogen Selenide.**—The methods for the preparation of hydrogen selenide,  $\text{H}_2\text{Se}$ , are very similar to those for hydrogen sulfide. It may be formed by the direct union of the elements or by acting upon ferrous selenide,  $\text{FeSe}$ , with hydrochloric acid.

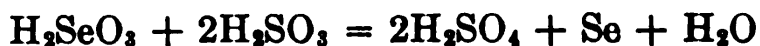


Hydrogen selenide resembles hydrogen sulfide in that it is a colorless poisonous gaseous substance soluble in water, giving an acid solution from which the element is deposited upon exposure to the air and further that it precipitates difficultly soluble selenides from solutions of salts of the heavy metals.

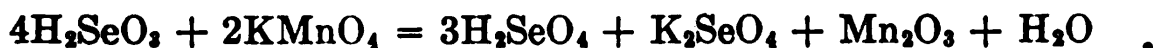
It is more easily liquefied (boiling-point  $-41^\circ$ ) than hydrogen sulfide and has a much worse odor resembling decayed horseradish.

**Selenium Dioxide and Selenious Acid.**—Selenium burns in air forming solid selenium dioxide,  $\text{SeO}_2$ , which will dissolve in water forming easily soluble crystalline selenious acid.

It is a weak dibasic acid resembling sulfurous acid. Like the latter it acts both as a reducing and an oxidizing agent, but differs in that its oxidizing power is much stronger than its reducing. It oxidizes sulfurous acid to sulfuric,



but reduces permanganate, being oxidized to selenic acid,  $\text{H}_2\text{SeO}_4$ ,



**Selenic Acid.**—There is no selenium compound corresponding to sulfur trioxide, but selenic acid is strictly analogous to sulfuric acid.

It is in general a more powerful oxidizing agent than sulfuric acid since it liberates chlorine from hydrochloric acid and dissolves gold, but curiously enough, it is without action upon either hydrogen sulfide or sulfur dioxide.

### TELLURIUM

Tellurium is decidedly rare. It occurs free but mostly as tellurides of gold, silver, lead and bismuth. Tellurium is more metallic in its characteristics than the other members of the sulfur family. It forms both amorphous and crystalline modifications; the latter has a silvery white metallic luster, a density of 6.3, melts at  $450^\circ$ , and boils at  $1,390^\circ$ . At  $1,750^\circ$  the molecular weight shows that the formula is  $\text{Te}_2$ . The crystalline modification is a slight conductor of electricity. The element combines directly with oxygen, the halogens and many of the metals.

**Hydrogen Telluride.**—Tellurium compounds are in general similar to those of sulfur and selenium, but differ in some important points.

Hydrogen telluride is prepared much as hydrogen sulfide and selenide are. It is colorless, gaseous, has a bad odor, boils higher ( $0^\circ$ ) than they, and is much less stable. Its solution in water is very feebly acid.

**Tellurium Dioxide.**—Tellurium burns in oxygen forming the dioxide which is a white, crystalline substance, slightly soluble in water. The solution does not redden litmus.

**Tellurous Acid.**—Tellurous acid,  $\text{H}_2\text{TeO}_3$ , is a white powder, slightly soluble in water but dissolved by either potassium hydroxide or strong acids. It then acts both as a base and as an acid, but is neither strongly acid nor basic; nothing which acts in both these ways is ever strong in either.

Tellurium trioxide, ( $\text{TeO}_3$ ) is known, but unlike sulfur trioxide it is totally indifferent toward water. Telluric acid ( $\text{H}_6\text{TeO}_6$  or  $\text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$ ), is a very weak acid with some basic properties.

It is a powerful oxidizing agent and, unlike selenic acid, attacks hydrogen sulfide or selenide.

## THE SULFUR FAMILY

	Sulfur	Selenium	Tellurium
Formula.....	$S_8-S_2$	$Se_8-Se_2$	$Te_8$
Melting-point.....	$120^\circ$	$217^\circ$	$450^\circ$
Boiling-point.....	$444.6^\circ$	$690^\circ$	$1,390^\circ$
Hydrogen compounds.....	$H_2S$	$H_2Se$	$H_2Te$
Melting-point.....	$-83^\circ$	$-68^\circ$	$-48^\circ$
Boiling-point.....	$-61^\circ$	$-41^\circ$	$0^\circ$
Oxidized.....	Easily	Very easily	Most easily
Dioxide.....	$SO_2$	$SeO_2$	$TeO_2$
State.....	Gaseous	Solid	Solid
Acid.....	$H_2SO_3$	$H_2SeO_3$	$H_2TeO_3$
State.....	Solution	Solid	Solid
Reducing agent.....	Good	Weak	Weak
Oxidizing agent.....	Weak	Strong	Strong
Trioxide.....	$SO_3$	.....	$TeO_3$
Acid.....	$H_2SO_4$	$H_2SeO_4$	$H_2TeO_4$
Oxidizing agent.....	Fair	Strong	Strong

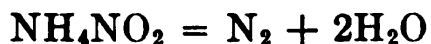
## CHAPTER XIV

### NITROGEN

**General.**—The element nitrogen occurs in nature both free and in combination. The free element is found in the air of which it constitutes approximately four-fifths by volume. The greater part of the remainder is oxygen. The element is decidedly inactive, but its compounds are among the most reactive of chemical substances. This will be seen at once when it is mentioned that they include gun cotton, nitroglycerine, and almost all of our modern high explosives. The inorganic compounds of nitrogen which occur in nature are principally ammonia, ammonia compounds, and salts of nitric acid. Large quantities of very complex carbon compounds of nitrogen are present in coal. Nitrogen compounds are of great importance to us, since it is with them that the vital phenomena seem to be directly connected. The albuminoids constitute an important class of such compounds, and contain almost 15 per cent. of nitrogen.

**Preparation of the Element.**—Impure nitrogen containing the members of the argon group can be obtained from air by burning phosphorus in the latter; or a product answering for many commercial purposes may be secured by the fractional distillation of liquid air; but the pure element can be obtained only by decomposing some nitrogen compound.

Ammonium nitrite,  $\text{NH}_4\text{NO}_2$ , when gently heated decomposes into water and nitrogen.



Ammonia and copper oxide, or nitric oxide,  $\text{NO}$ , and copper react at higher temperatures and yield pure nitrogen.

**Physical Properties.**—Nitrogen is a colorless, tasteless, odorless gas, which is very slightly soluble in water; 100 volumes of the latter dissolve 1.6 volumes of nitrogen. The density of nitrogen from chemical sources is 0.0012508, while that of the atmospheric

nitrogen is 0.00125718. It was this difference in density of the gas from the two sources that led to the discovery of argon. The critical temperature of nitrogen is  $-146^{\circ}$  and the critical pressure is 35 atmospheres. Its boiling-point is  $-195^{\circ}$ . The liquid nitrogen is colorless and has a density, at its boiling-point, of 0.8103. At  $-210^{\circ}$ , nitrogen freezes to a white solid.

The molecular weight of nitrogen is 28, and therefore, since its atomic weight is 14.01, its formula is  $N_2$ .

**Chemical Properties.**—Toward most of the other elements, nitrogen ordinarily shows itself to be inactive. At higher temperatures, or under the influence of the electric glow discharge it becomes fairly active. When the gas is passed over strongly heated lithium, magnesium, calcium, or boron, direct combination takes place with the formation of the nitrides of these elements,  $Li_3N$ ,  $Mg_3N_2$ ,  $Ca_3N_2$ , and  $BN$ . A mixture of powdered lime (calcium oxide,  $CaO$ ) and magnesium reacts so vigorously when heated in a current of nitrogen that the phenomena strongly resemble those of combustion of many substances in oxygen.

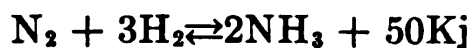
When nitrogen is mixed with either oxygen or hydrogen and heated, but little action takes place. When an electric spark is passed through either of these mixtures, some change occurs, but soon comes to an end since the reactions are reversible. In the case of nitrogen and oxygen, nitric oxide,  $NO$ , is first formed and this then combines with the excess of oxygen present to form nitrogen peroxide,  $NO_2$ . The nitrogen and hydrogen unite to form ammonia,  $NH_3$ . Nitrogen rendered active by the electric glow discharge will continue to glow for some time after the discharge has ceased, and will react with phosphorus, sodium, mercury, and with some compounds of carbon and hydrogen. In many respects it seems to be analogous to ozone, but is less stable than the latter.

**Hydrogen Compounds of Nitrogen.**—By far the most important of the compounds of hydrogen and nitrogen is ammonia,  $NH_3$ . Some idea of its importance may be gained from the fact that the yearly production of the compound and its salts is equal to 260,000 tons of ammonia. In addition to ammonia we have the less important compounds, hydrazine,  $N_2H_4$ , and hydronitric acid,  $HN_3$ .

**Ammonia—Occurrence.**—Ammonia is present in very small quantities in the air and in all river and rain waters, both as uncombined ammonia and as ammonium nitrate,  $\text{NH}_4\text{NO}_3$ , and ammonium nitrite,  $\text{NH}_4\text{NO}_2$ .

**Preparation.**—Ammonia may be prepared directly from the elements under the influence of an electric spark, or better, by heating a highly compressed mixture of nitrogen and hydrogen to not over  $750^\circ$  in the presence of finely divided iron or uranium as catalyzer.

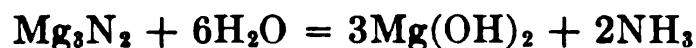
An application of the law of mobile equilibrium to the equation for the reaction



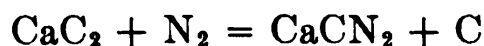
shows that since the volume of the ammonia is less than that of the elements, high pressure is favorable; while the evolution of heat indicates that ammonia will decompose with rising temperature, and therefore a low temperature will lead to a more complete union of the elements.

This reaction is now being used for the synthesis of ammonia on a large scale. The pressure used is about 200 atmospheres and one of the chief problems is to keep the apparatus gas-tight at the high pressure and temperature necessary.

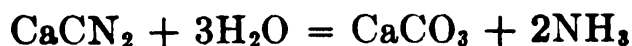
Water acts upon nitrides forming ammonia and the hydroxide of the metal. The equation for the decomposition of magnesium nitride is given below:



A somewhat analogous method consists in the formation of calcium cyanamide,  $\text{CaCN}_2$ , by the action of nitrogen upon calcium carbide,  $\text{CaC}_2$ , at fairly high temperatures:



Water decomposes this calcium cyanamide and yields calcium carbonate,  $\text{CaCO}_3$ , and ammonia,



These reactions are the basis of a thoroughly practical process for obtaining ammonia from the nitrogen of the air and are now being carried out on a very large scale.

Animal refuse including horns, hides, hair, feathers, etc., when heated gives off a part of the nitrogen in the form of ammonia. A solution of ammonia in water was formerly prepared

in this way and was known as spirits of harts-horn; a name that is sometimes used at the present day. Some ammonia is given off from volcanoes and collects around them in the form of ammonium chloride,  $\text{NH}_4\text{Cl}$ .

Coal contains upward of 2 per cent. of nitrogen in combination with carbon, hydrogen, etc.; and when the coal is heated in the absence of air, as in the manufacture of coal gas, and in some of the methods for making coke, a part of this nitrogen is given off in the form of ammonia. The gases are led through water which dissolves the greater part of the ammonia and also many other substances. This "ammoniacal liquor" is then mixed with slaked lime and heated. The ammonia is given off and absorbed in dilute hydrochloric acid or sulfuric acid, forming ammonium chloride,  $\text{NH}_4\text{Cl}$ , or ammonium sulfate,  $(\text{NH}_4)_2\text{SO}_4$ . The greater part of the ammonia of commerce is prepared from coal in this way.

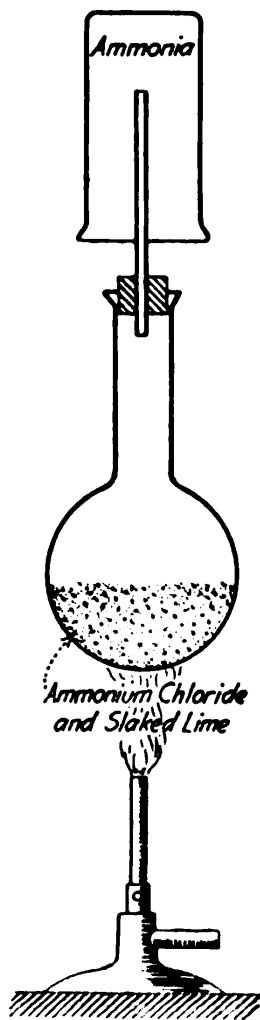
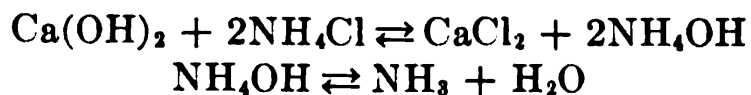


FIG. 33.

In the laboratory, ammonia is usually obtained by gently heating a mixture of slaked lime,  $\text{Ca}(\text{OH})_2$  and ammonium chloride (Fig. 33). Ammonium hydroxide is first formed and then decomposed into ammonia and water.



It may also be secured by heating a strong aqueous solution of ammonia.

Ammonia cannot be dried by either sulfuric acid or calcium chloride, since it forms ammonium sulfate with the one and a compound,  $\text{CaCl}_2 \cdot 8\text{NH}_3$ , which strongly resembles a salt with water of crystallization, with the other. Unslaked lime,  $\text{CaO}$ , or potassium hydroxide is used to dry the ammonia.

**Physical Properties.**—Ammonia is a colorless gaseous substance whose molecular weight is 17.034. It has a very strong characteristic odor which is familiar to everyone.

Its solubility in water is exceedingly great, one volume at room temperature takes up 800 times its volume, or 0.6 of its weight of ammonia. At zero degrees, water will dissolve even more of the gas. In spite of the great solubility of ammonia, it still follows Henry's law approximately, especially at higher temperatures.

The critical pressure of ammonia is 111 atmospheres, and its critical temperature is  $132^{\circ}$ . It may therefore be liquefied by pressure alone at ordinary temperatures. The boiling-point is  $-33.5^{\circ}$ . It is a colorless, very mobile liquid which freezes to a white, crystalline solid at  $-77^{\circ}$ . The density of the liquid at its boiling-point is 0.677. The liquid ammonia is a very good solvent indeed for many substances, including a large number of salts. When salts are dissolved in liquid ammonia, they are dissociated very much as they are in water, though to a smaller degree at any given concentration than when dissolved in water. The ions travel faster in ammonia than in water, so that solutions of salts in ammonia are often better conductors of electricity than aqueous solutions of the same salts.

Liquid ammonia is a very common article of commerce, compressed in strong iron cylinders. The greater part of this is used in plants for the manufacture of ice and for cold storage. Its use for such purposes depends upon the fact that, like all other liquids, it absorbs a great amount of heat when it evaporates—the "heat of vaporization" as it is called. The ammonia does not enter into the ice in any way, but is simply used as a carrier of heat from a lower to a higher temperature. Such a process is not a spontaneous one, and can be brought about only by the expenditure of work. The process may be briefly outlined as follows:

The gaseous ammonia is compressed, generally by a steam driven pump (Fig. 34), until it liquefies in a coil of iron pipes cooled by a stream of water. In liquefying, it gives out to the water the heat of condensation. The liquefied ammonia is then allowed to escape into another coil of pipes, called the expansion coil, in which it evaporates, thereby taking up from its sur-

roundings the heat of evaporation. The gaseous ammonia passes back from the expansion coil to the pump where it is re-compressed and liquefied, giving up the heat absorbed in evaporating. It then passes once more into the expansion coil and so is kept circulating through the system. The expansion coil is usually immersed in brine which is cooled by the evaporating ammonia to temperatures below the freezing-point of water. Manufactured ice is made by placing cans containing about 200 lb. of distilled water in the brine and letting them stand until the water is all frozen. The ice prepared in this way is very pure, and much superior to most natural ice for domestic purposes.

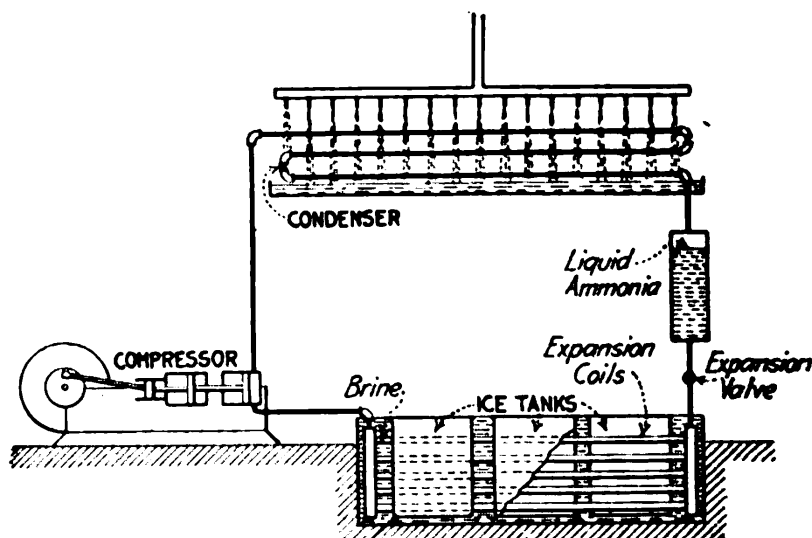


FIG. 34.

As was mentioned above, the ammonia simply serves to carry the heat from a lower to a higher temperature at the expense of the work done by the engine. Any other very easily volatile liquid might be used instead of the ammonia, and several others have been so employed.

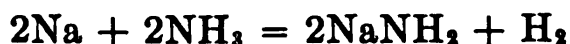
**Chemical Properties of Ammonia.**—When ammonia is heated by electric sparks or otherwise, the reverse of the reaction for its synthesis (see p. 193) takes place and it is largely decomposed into its elements. The decomposition is more complete the lower the pressure and the higher the temperature.

Ammonia will burn in oxygen but not in air. It burns with a pale yellow flame forming water, nitrogen, ammonium nitrite,  $\text{NH}_4\text{NO}_2$ , and ammonium nitrate,  $\text{NH}_4\text{NO}_3$ . In the presence of a suitable catalyzer, platinum for example, ammonia will react

t a moderate rate with oxygen of the air to form nitric acid. This is the basis of what is known as the Ostwald process of making nitric acid.

When ammonia is passed over heated copper oxide or other easily reducible oxide, the metal, water, and nitrogen are usually obtained.

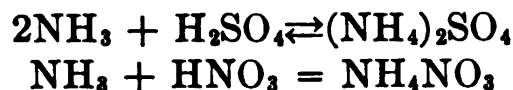
When dry ammonia is passed over heated potassium or sodium, hydrogen and potassium or sodium amide,  $\text{KNH}_2$  or  $\text{NaNH}_2$  are formed:



The most prominent chemical property of ammonia is its ability to combine directly with acids for the formation of ammonium salts. For example, with hydrogen chloride, it forms dense white fumes of ammonium chloride:



With other acids the action is very similar as shown by the following equations:



Most of these salts, when heated to a sufficiently high temperature, break down into ammonia and the acid from which they were formed, just the reverse of the above process. Ammonium nitrate and nitrite are exceptions. The decomposition of ammonium nitrite into nitrogen and water has already been given. The nitrate decomposes into nitrous oxide,  $\text{N}_2\text{O}$ , and water,



When ammonia dissolves in water, a part of it combines with the formation of ammonium hydroxide,  $\text{NH}_4\text{OH}$ ,



The reaction is reversible, and only a portion of the substances are present as hydroxide. At a temperature of  $-79^\circ$ , ammonium hydroxide may be prepared as a white crystalline solid. Another crystalline compound of ammonia and water can be obtained at

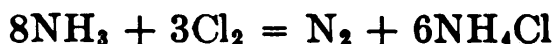
a low temperature. It has the composition  $(\text{NH}_4)_2\text{O}$ , and may be called ammonium oxide. Its freezing-point is  $-79^\circ$ .

Ammonium hydroxide is a weak base and in normal solution is dissociated to the extent of about 0.4 per cent. The ions are hydroxyl and ammonium,  $\text{NH}_4^+$ . This ammonium ion has many properties which are very similar to those of the potassium ion.

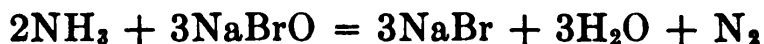
Upon neutralizing ammonium hydroxide with acid and evaporating the solution, salts are obtained which are identical with those formed by direct union of the acids and ammonia. These salts like other salts, are highly dissociated when dissolved in water. With solutions of strong bases, they at once react, forming undissociated ammonium hydroxide which then breaks down into the ammonia and water as was shown in the discussion of the preparation of ammonia. This reaction is used for the recognition of ammonium compounds. The ammonia is detected by its action on wet litmus, by the white fumes formed with hydrochloric acid, and even by its odor.

Ammonium salts, especially the sulfate and chloride, are much used as fertilizers to supply the necessary nitrogen for the growth of plants. The greater part of the 1,000,000 tons of ammonium salts which are annually produced is used as fertilizer.

An excess of ammonia reacts with chlorine or bromine forming ammonium salts and nitrogen. The equation for the reaction with chlorine is given below; that for bromine is similar:

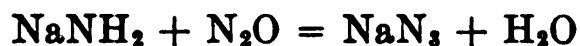


Hypobromites and hypochlorites act upon ammonia in such a way that all the nitrogen is set free in the gaseous state:



**Hydrazine.**—Hydrazine,  $\text{N}_2\text{H}_4$ , is a colorless liquid which boils at  $114^\circ$  and freezes at  $1^\circ$ . It combines with water yielding a hydrate,  $\text{N}_2\text{H}_6\text{O}$ , which is volatile without decomposition. It will react with acids with the formation of salts. Two series of such salts are known,  $\text{N}_2\text{H}_5\text{A}$  and  $\text{N}_2\text{H}_6\text{A}_2$ , in which A stands for any anion carrying one negative charge. Hydrazine is formed by the reduction of nitrogen compounds and is itself a very strong reducing agent.

**Hydronitric Acid or Hydrazoic Acid.**—The sodium salt of hydronitric acid or hydrazoic acid, as it is often called, may be prepared by the action of nitrous oxide,  $N_2O$ , upon sodium amide,  $NaNH_2$ :



From this salt, the acid is prepared by distillation with dilute sulfuric acid. It is a colorless liquid with a strong and very disagreeable odor. It boils at  $37^\circ$  and explodes violently on contact with hot objects. The substance sometimes explodes at ordinary temperatures, thus making it very dangerous to handle.

It is a rather weak acid though somewhat stronger than acetic acid. Its salts resemble the chlorides except that the salts of the heavy metals are explosive and the difficultly soluble silver salt is soluble in the stronger acids, while the chloride is not.

**Air.**—Air is a mixture of a rather large number of gaseous substances and in addition always contains some floating particles of dust. The main gaseous constituents which are present in almost fixed proportions are nitrogen, oxygen and members of the argon group; in addition, it contains variable amounts of water vapor, carbon dioxide, and ammonia. In the neighborhood of cities and chemical works sulfur dioxide, hydrogen sulfide, hydrochloric acid and a few other gases are found. These may be regarded as impurities and neglected in the discussion of air.

The quantity of carbon dioxide varies from about 3 to 4 parts per 10,000 in the air of the country to 6 to 7 parts in the cities and in badly ventilated rooms may run up to 50 parts. This carbon dioxide is formed during the burning or decay of any carbonaceous materials, and is also given off during the breathing of animals. It is however taken up by green plants, and with the aid of the energy absorbed from the light of the sun, is utilized in building up the various plant tissues, oxygen being set free at the same time. This tends to keep the carbon dioxide content of the air approximately constant.

**Composition of the Air.**—The quantity of water vapor present in the air is so variable that no definite statement concerning it can be made, but the composition of dry air is shown in the following table:

## Dry Air contains:

Per cubic meter	Per kilogram
781.3 liters nitrogen.....	755.14 grm.
209.9 liters oxygen.....	231.47 grm.
9.4 liters argon, etc.....	12.92 grm.
0.3 liters carbon dioxide.....	0.46 grm.
0.1 liters hydrogen.....	0.01 grm.

The term argon, etc., includes argon, helium, neon, krypton and xenon.

In spite of the many factors which tend to change the composition of the air, the winds produce such a thorough mixing that its composition remains practically fixed, although measurable variations do occur.

The density of dry air is 0.001293 under standard conditions. In contact with water, each gas dissolves in proportion corresponding to its solubility and its partial pressure as described by Henry's law. The solubility of oxygen is so much greater than that of nitrogen that in spite of its smaller partial pressure relatively more oxygen than nitrogen dissolves.

**Liquid Air.**—The critical temperature of air is  $-140^{\circ}$  and its critical pressure about 39 atmospheres. Liquid air boils from  $-194^{\circ}$  to  $-185^{\circ}$  according to its composition, and when first prepared contains from 28 to 50 per cent. of oxygen. As it stands, the nitrogen (boiling-point  $-195^{\circ}$ ) tends to pass off first and leaves the oxygen (boiling-point  $-182.5^{\circ}$ ) behind. This is made the basis of very practical methods for obtaining both oxygen and nitrogen from the air sufficiently pure for many commercial purposes. Liquid nitrogen has a smaller density than that of water, while the reverse is the case with liquid oxygen. Liquid air when freshly prepared is specifically lighter than water, but on partial evaporation becomes heavier. The color also changes from practically colorless to the blue of liquid oxygen.

To liquefy air it is first partially freed from carbon dioxide by slaked lime, and then compressed to 150 to 200 atmospheres. A great deal of heat is developed in this process so the gas is cooled to ordinary temperatures by water in the jackets around the compressor (Fig. 35), and by passing it through a coil surrounded by water. The greater part of the water vapor in the air condenses at this high pressure and the remainder together

with the rest of the carbon dioxide is removed by potassium hydroxide. The purified highly compressed air then enters the liquefier at the temperature of the room. The liquefier consists of a coil of very small copper tubing carrying at its lower end a valve for controlling the flow of the air. The whole is inclosed in a metal jacket and thoroughly insulated from its surroundings by wool. Through the copper tube, the air flows in a continuous stream and as it escapes from the valve at the lower end of the

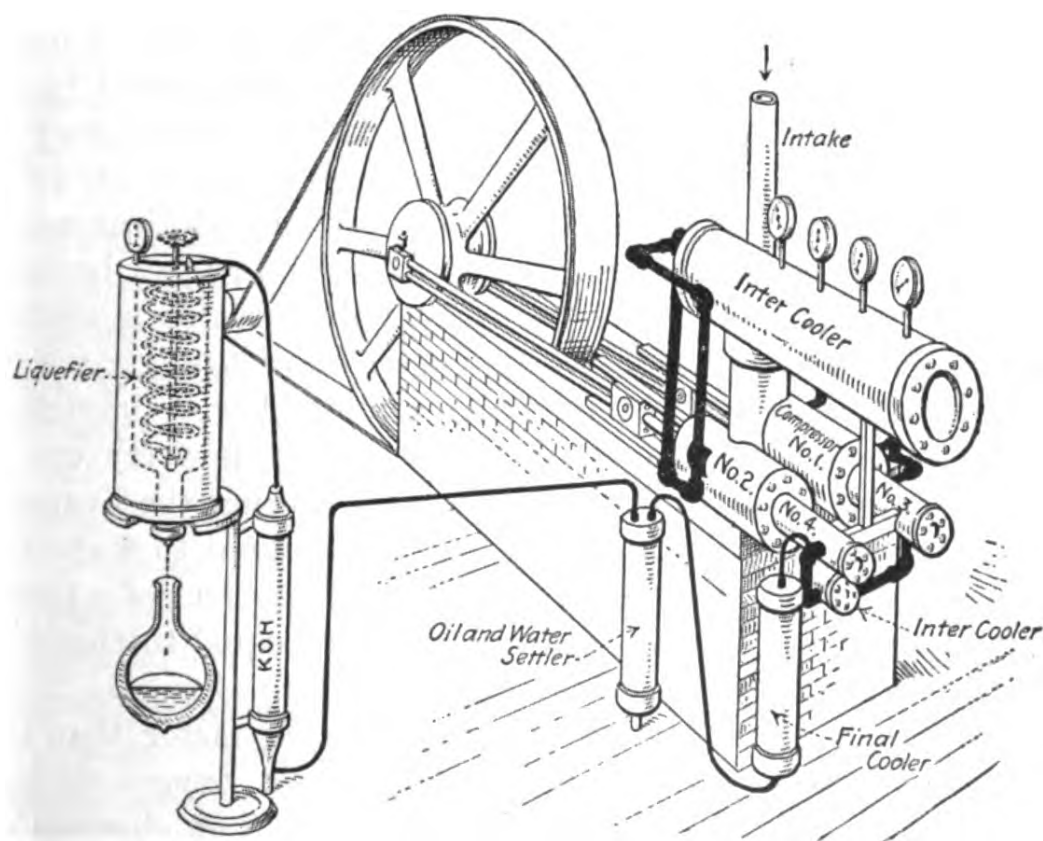


FIG. 35.

coil, it becomes somewhat cooler. By the construction of the apparatus, this cooled air is compelled to pass up over the coil thereby cooling it together with the oncoming air which reaches the valve at a lower temperature than the first of the stream, and in expanding becomes still cooler and in turn lowers the temperature of the coil. This process goes on until a few minutes after starting the machine the temperature has been so far lowered that about 5 per cent. of the air issuing from the expansion valve is liquefied. The rest is returned to the machine, recompressed and sent around the cycle once more. In large plants part of the cooling is accomplished with carbon dioxide and ethylene.

The liquid air must not be corked up and will evaporate as rapidly as it can get the necessary heat, so after it is obtained it is preserved in double-walled vacuum-jacketed vessels which are usually coated on the inside of the walls with silver. Such vessels are very good heat insulators indeed.

Liquid air on account of its low boiling-point is an exceedingly useful substance for investigations at low temperatures.

**Experiments.**—Many interesting and striking experiments may be performed with liquid air. These depend essentially upon two properties; first that it has a very low boiling-point, and second that it is a source of oxygen. When cooled to the temperature of liquid air, most of the familiar gases such as chlorine, hydrogen chloride, hydrogen bromide, ammonia, sulfur dioxide, methane and hydrogen sulfide become odorless solids. Liquids such as alcohol and kerosene freeze, and rubber becomes as brittle as glass and may be easily pulverized in a mortar. Metals such as copper and steel become a third stronger toward a steady pull, but break readily under a quick blow. Crystalline metals, on the other hand, are distinctly weaker in every way at this low temperature. The heat absorbed during the evaporation of 1 grm. of liquid air plus the heat required to warm the gaseous air to  $0^{\circ}$  is about 80 cal., so the cooling effect of a pound of liquid air in a refrigerator would be about equal to that of a pound of ice.

When liquid air boils, the nitrogen goes off faster than the oxygen, and after a time almost pure liquid oxygen is left. This furnishes oxygen of such concentration that charcoal or steel will burn with exceeding brilliancy in the liquid. Cotton or charcoal wet with just the proper amount of oxygen to complete the combustion will explode when set off with a mercury fulminate cap with the violence of an equal weight of dynamite. Aluminum powder made into a paste with liquid oxygen will burn with a blinding flash upon contact with a flame, and the temperature of the mass is changed in a small fraction of a second from  $183^{\circ}$  below to something like  $3,000^{\circ}$  above zero.

**Air is a Mixture.**—That air is a homogeneous mixture and not a chemical compound is shown by several arguments.

1. Nitrogen and oxygen may be mixed in the proportion in which they are present in the air, and no heat effect will result,

no changes in volume, nor any other evidence of chemical transformation and yet the mixture behaves like air in every respect.

2. The composition of the air varies while that of a compound is perfectly fixed.

3. Relatively more oxygen than nitrogen is dissolved by water, while a compound dissolves as a whole, without any change in the proportions of the components.

4. The properties of the air are a mean of the properties of its components, which would not be true if it were a compound.

5. The separation of the gases by liquefaction and fractional distillation indicates a mixture.

**Air and Life.**—Oxygen is absolutely indispensable for the continuance of all forms of animal life. The purely aquatic forms get their oxygen from air dissolved in the water, while the rest breathe the air directly. We, for example, take in about half a liter of air at each breath, and remove from this about 5 per cent. of the oxygen, giving to it about 3.7 per cent. of carbon dioxide. The nitrogen is unchanged. The oxygen taken up in the lungs largely enters into a loose combination with a substance called hemoglobin in the red corpuscles of the blood and is carried to all parts of the body, gradually oxidizing the various body substances, chiefly to carbon dioxide, water, and fairly simple compounds of carbon, nitrogen, hydrogen, and oxygen. The carbon dioxide is largely given up by the blood to the air upon its return to the lungs. The oxidation of these substances is the source of the body heat, and of the energy which we spend as work.

**Oxides and Oxyacids of Nitrogen.**—There are five oxides of nitrogen. Three of these are anhydrides of acids. The names and formulas of these oxides are given in the following table with the names and formulas of the acids opposite their anhydrides.

Nitrous oxide or hyp-		
nitrous anhydride.....	$N_2O$	Hyponitrous acid..... $H_2N_2O_2$
Nitric oxide.....	$NO$	.....
Nitrogen trioxide or		
nitrous anhydride.....	$N_2O_3$	Nitrous acid..... $HNO_2$
Nitrogen peroxide.....	$NO_2$ or $N_2O_4$	.....
Nitrogen pentoxide or		
nitric anhydride.....	$N_2O_5$	Nitric acid..... $HNO_3$

**Nitric Acid.**—Nitric acid, the most important of the oxyacids, does not occur free in nature, but its salts are present in all fertile soils. Potassium nitrate,  $\text{KNO}_3$ , has been known for centuries under the name of saltpeter. The sodium salt,  $\text{NaNO}_3$ , occurs in great deposits in the desert regions of Chile, and hence is called Chile saltpeter. Enormous quantities of this are extracted and shipped all over the world for use in preparing other nitrogen compounds, and as a fertilizer.

Under the influence of electrical discharges nitrogen, oxygen, and water will combine for the formation of nitric acid, and this, together with the ammonia of the air, is doubtless the source of the ammonium nitrate contained in rain water.

Certain forms of soil bacteria are able to convert ammonia and nitrogenous organic substances into nitric acid the latter then reacts with the calcium carbonate of the soil to form calcium nitrate,  $\text{Ca}(\text{NO}_3)_2$ .

Nitric acid is prepared by the first general method by distilling sodium nitrate with sulfuric acid in cast-iron retorts. Enough sulfuric acid is used to make the sodium acid sulfate which is either sold as such or heated with sodium chloride to make hydrochloric acid and the neutral sulfate.



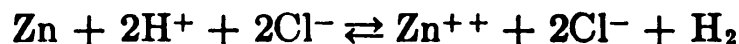
Pure nitric acid is a colorless liquid having a density of 1.53 at 15°. It boils at 86°. It gradually decomposes, especially under the influence of light into oxygen, water, and oxides of nitrogen, which color the acid yellow. The addition of water makes the acid much more stable. The conductivity of the pure solution is much greater than that of the pure acid which indicates that the water has changed the acid into ions. This may account for the increased stability. As water is added to the acid, the boiling-point gradually rises until when a 68 per cent. acid is formed, the boiling-point reaches a maximum at 120°. The relations here are very similar to those between hydrochloric acid and water.

**Chemical Properties of Nitric Acid.**—The chief chemical properties of nitric acid depend upon the fact that it is both a strong acid and very powerful oxidizing agent.

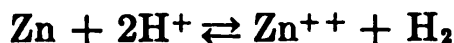
As an acid it is as strong as any, being as highly dissociated

into its ions at any given dilution as hydrochloric acid. Consequently it is able to do anything that depends upon the concentration of the hydrogen ions, which any other acid can do.

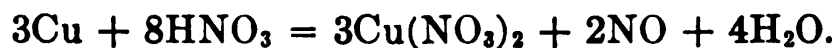
As will be recalled, the ordinary reaction between an acid and a metal whereby the metal is dissolved and hydrogen is liberated is regarded as taking place between the metal and the hydrogen ion, and as consisting of the oxidation of the metal to its ion and the reduction of the hydrogen ion to the free element. For example, in that between zinc and hydrochloric acid, the chlorine ion is considered to take no part, the entire reaction being between the zinc and the hydrogen ion,



or, leaving out the idle chlorine ion,



Nitric acid being a strong acid its hydrogen ion is as well able to oxidize metals as hydrochloric and in addition, because of its being a nitrate, nitric acid is able to oxidize and dissolve copper, mercury, and silver which hydrochloric cannot do. It cannot be too strongly emphasized that in the case of these last-mentioned metals hydrogen is *not* given off, but in its place nitric oxide appears. The nitrogen in nitric acid, in which it has a valence of 5 positive, has a great tendency to pass into nitric oxide in which it has a valence of 2 positive, and in so doing exerts a very powerful oxidizing action, much more so than the hydrogen ion and consequently is able to oxidize copper, mercury and silver which hydrogen as ion cannot do. The equation for the action on copper is as follows:



In the discussion of the halogens, it was pointed out that concentrated sulfuric acid is a rather powerful oxidizing agent. It is much stronger than the hydrogen ion and will oxidize copper, mercury, and silver to their ions. As with nitric acid, hydrogen gas is not evolved, but an oxide, sulfur dioxide in this case, is given off. Here again we have a change in valence, for the sulfur in sulfuric acid is 6 positive and in sulfur dioxide 4

positive. The equation for the reaction between sulfuric acid and copper is:



As has been pointed out, a change of valence such as we have just mentioned is an essential accompaniment of oxidation.

Gold and platinum are not oxidized by nitric acid in the absence of chlorine as ion, and therefore this acid is used in the refining of these metals to dissolve the silver, etc., with which they may be alloyed. Because of the vigor of its action on metals, nitric acid was formerly called *aqua fortis*.

In addition to its use as indicated above, nitric acid is largely employed in the laboratory and in the manufacture of nitrates, dyestuffs, sulfuric acid, nitroglycerine, guncotton, etc.

**Aqua Regia.**—Aqua regia is a mixture of nitric and hydrochloric acids, and is capable of attacking gold and platinum, metals which do not dissolve in either of these acids alone. The action is not due to aqua regia's being primarily a stronger oxidizing agent than the nitric acid but to the fact that the chlorides of gold and platinum are much more stable than their nitrates and in aqua regia, the chlorides of the metals may be formed. This increased stability of the chloride over the nitrate materially assists in the oxidation of the metals and is enough to enable the nitrate to do the work, but not sufficient to cause the hydrogen ion from hydrochloric acid to oxidize the gold or platinum.

Aqua regia received its name long ago when the alchemists found that it was a solvent for gold which they considered to be the king of metals.

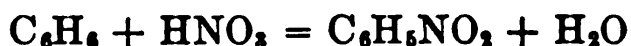
When aqua regia is heated alone, it gives off chlorine and compounds of nitrogen, oxygen, and chlorine; one of these is nitrosyl chloride, NOCl.

**Nitrates.**—Nitric acid, as is indicated by its formula, is a monobasic acid and yields only one series of salts, the nitrates. These are formed by the action of the acid upon the metals or bases.

These salts are all readily soluble in water. The nitrates are decomposed rather easily at elevated temperatures, generally giving oxygen, oxides of nitrogen, and the oxide of the metal. Most of the applications of nitrates depend upon their action as oxidizing agents. When heated with charcoal they often

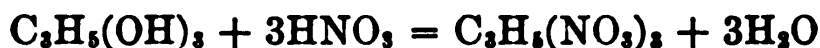
letonate. Potassium nitrate, charcoal, and sulfur in the proper proportions constitute gunpowder.

**Nitro Compounds.**—Very concentrated nitric acid acts upon compounds of carbon and hydrogen forming nitro-compounds and water. For example, nitric acid and benzene,  $C_6H_6$ , react for the formation of nitrobenzene,  $C_6H_5NO_2$ , and water.



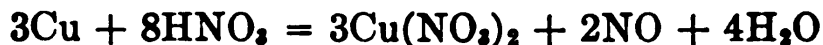
The group  $NO_2$  is known as the nitro group. The water formed in the reaction is detrimental, so concentrated sulfuric acid is mixed with the nitric acid to take up this water.

Alcohols (carbon, hydrogen and oxygen compounds containing hydroxyl) react with nitric and sulfuric acids for the formation of compounds which in their formulas are similar to nitrates, but which are not salts. Glyceryl nitrate or nitroglycerine,  $C_3H_5(NO_3)_3$ , is formed by the action of this mixture of acids upon an alcohol called glycerine,  $C_3H_5(OH)_3$ :



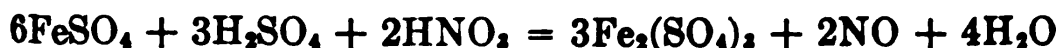
**Nitrogen Pentoxide.**—Nitrogen pentoxide  $N_2O_5$  is a colorless, mobile, very volatile liquid which soon passes over into a white crystalline solid, melting at  $30^\circ$ . It is made by distilling a mixture of phosphorus pentoxide and nitric acid. It is the anhydride of nitric acid.

**Nitric Oxide.**—Nitric oxide,  $NO$ , is formed by the action of somewhat dilute nitric acid, sp. gr. 1.2, upon copper, as shown in the following equation:



The gas so obtained is never pure, since it always contains some nitrous oxide,  $N_2O$ , and often nitrogen.

The pure oxide may be obtained by adding nitric acid to a boiling solution of ferrous sulfate,  $FeSO_4$ , in dilute sulfuric acid. The equation is as follows:



The ferrous sulfate is oxidized to ferric sulfate,  $Fe_2(SO_4)_3$ , and the nitric acid reduced to nitric oxide.

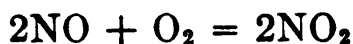
**Properties of Nitric Oxide.**—Nitric oxide is a colorless gas whose molecular weight is 30 corresponding to its formula  $NO$ .

It is only slightly soluble in water. The critical temperature of the gas is  $-93^{\circ}$ , and its boiling-point is  $-150.2^{\circ}$ . So it is more like the so-called permanent gases, oxygen, hydrogen, etc., than most of the gaseous substances which we have been discussing.

Nitric oxide is the most stable toward heat of the oxides of nitrogen. Even when heated to a temperature of  $2,000^{\circ}$  only about 1 per cent. of it is decomposed. In fact it is formed from its elements at very high temperatures, and may be obtained by passing the electric spark through air. This is made the basis of a successful method for the preparation of nitric acid and nitrates on a commercial scale as will be explained later.

Briskly burning wood or phosphorus continues to burn in nitric oxide. The flame is about as bright as when the combustion takes place in oxygen. Most other burning substances, for example a candle or sulfur, are extinguished. Since the heat of formation of nitric oxide is  $-90$  KJ. considerable heat is evolved in its decomposition, and a given quantity of a substance like phosphorus burning in NO will liberate more heat than if it had burned in oxygen.

Nitric oxide combines directly with oxygen at ordinary temperatures, forming the reddish-brown nitrogen peroxide,  $\text{NO}_2$ :



This nitrogen peroxide is at once formed whenever the nitric oxide comes in contact with the air, consequently it is impossible to say anything about the odor of nitric oxide.

Nitric oxide is soluble in solutions of ferrous salts with the production of a dark brown solution containing  $\text{FeNO}^{++}$ . From this solution the oxide is driven out by heating to the boiling-point. In this way pure NO may easily be obtained from mixtures with other gases, since the latter are either not absorbed in the first place or are retained when the solution is boiled.

The formation of this dark colored solution may be utilized as a test for nitric acid, a nitrate, or in general any oxygen compound of nitrogen higher than nitric oxide. The equation for the reduction of nitric acid to nitric oxide is given on page 207.

**Nitrogen Peroxide.**—Nitrogen peroxide as has already been mentioned is formed by the direct union of oxygen and nitric oxide. It may also be prepared by heating certain nitrates.

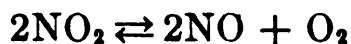
Lead nitrate, for example, decomposes to give nitrogen peroxide, oxygen, and lead oxide, as shown by the following equation:



It condenses to a yellowish-red liquid which boils at  $22^\circ$  and at low temperatures freezes to an almost colorless solid, melting at  $-12^\circ$ .

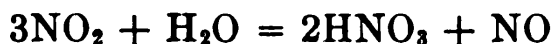
The molecular weight of the gaseous compound varies with the conditions of temperature and pressure under which it is determined. At low temperatures and rather high pressures it is nearly 92, corresponding to a formula for the compound of  $\text{N}_2\text{O}_4$ . As the temperature is raised and the pressure diminished, the molecular weight gradually falls until it reaches a limit of 46, corresponding to the formula  $\text{NO}_2$ . This change from one form to the other is accompanied by a marked change in color. At rather low temperatures the gas has a yellow-brown color, as the temperature is raised it becomes darker and darker until at  $154^\circ$  it has reached such a deep black-red that it is almost opaque, even in thin layers.

When nitrogen peroxide is heated above  $154^\circ$ , it gradually loses its dark color as the temperature rises, and finally becomes colorless. This color change is due to the transformation of  $\text{NO}_2$  into  $\text{NO}$  and oxygen.

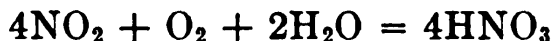


This decomposition becomes practically complete at  $620^\circ$ .

Nitrogen peroxide reacts with water to form nitric acid and  $\text{NO}$ ,



In the presence of air,  $\text{NO}$  will pass into  $\text{NO}_2$ , which in turn will form more nitric acid. So the reaction of  $\text{NO}_2$ , air, and water will ultimately yield the whole of the nitrogen in the form of nitric acid.



**Nitric Acid from the Air.**—When air is passed through an electric arc, its temperature becomes extremely high, and a small quantity of nitrogen and oxygen unite to form nitric oxide. When this has cooled sufficiently, it unites with oxygen to form

nitrogen peroxide; which then will react with water and oxygen as shown in the preceding section to form nitric acid. This process has recently become of great importance and is carried out at many places, but one of the largest plants is at Notodden, Norway. Here the arc is formed by a high potential alternating current between copper electrodes which are placed at right angles to the poles of a powerful electromagnet. Under these conditions the arc is forced to move rapidly alternately up and down according to the direction of the current so that it appears to form a flat disc of electric flame (Fig. 36) through which the

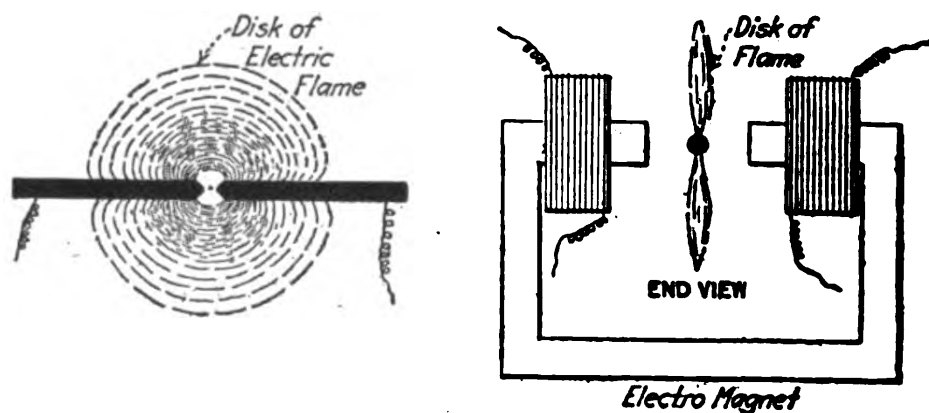
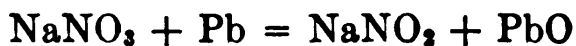


FIG. 36.

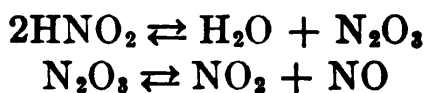
air passes. The oxides of nitrogen formed are taken up by water in towers similar to the Glover or Gay Lussac towers, and the nitric acid is either concentrated and used in this form, or is converted into calcium nitrate by letting it act upon slaked lime.

The calcium nitrate is a good fertilizer and is put on the market at a low enough price to compete with the Chile saltpeter.

**Nitrites.**—When potassium or sodium nitrates are heated, especially in the presence of a reducing agent like lead, they lose one atomic weight of oxygen per mole and are changed into nitrites,



When an acid is added to a strong solution of a nitrite, the nitrous acid formed breaks up immediately into water and nitrous anhydride,  $\text{N}_2\text{O}_3$ ; but the latter at once almost completely decomposes into nitrogen peroxide and nitric oxide,



in this way a nitrite is easily distinguished from a nitrate, since the nitrogen peroxide is so highly colored.

Nitrous acid oxidizes good reducing agents while it is itself oxidized by strong oxidizing agents. For example, it oxidizes HI, and reduces potassium permanganate,  $\text{KMnO}_4$ . The nitrites are largely used in the manufacture of organic dyes.

**Nitrous Anhydride.**—Besides the method just given for the formation of nitric oxide and the peroxide in the preparation of nitrous anhydride, this same mixture may be obtained by heating arsenic trioxide,  $\text{As}_2\text{O}_3$ , with nitric acid having a density of 1.30 to 1.35. The arsenic trioxide is oxidized to the pentoxide,  $\text{As}_2\text{O}_5$ , and the nitric acid reduced to nitrous which at once breaks down into water and the mixture of the two oxides. This mixture of the two oxides may be condensed by a freezing mixture to a dark-blue liquid which boils at  $3.5^\circ$ . If the liquid is completely dried, it may then be vaporized without dissociating. So dry nitrous anhydride,  $\text{N}_2\text{O}_3$ , can exist while the moist compound cannot.

**Hyponitrites and Hyponitrous Acid.**—Sodium hyponitrite,  $\text{Na}_2\text{N}_2\text{O}_2$ , may be made by reducing sodium nitrite with sodium amalgam. From this hyponitrous acid may be made. It is a solid which decomposes irreversibly into water and nitrous oxide  $\text{N}_2\text{O}$ ; hence the latter is often called hyponitrous anhydride.

**Nitrous Oxide.**—Nitrous oxide is readily prepared by heating ammonium nitrate, which decomposes into this substance and water,



It is a colorless gaseous substance which has a faint odor and is fairly soluble in cold water. At room temperatures, water will dissolve about its own volume of the oxide. Its critical pressure is 75 atmospheres and its critical temperature  $+36^\circ$ ; so it is easily liquefied by pressure alone at ordinary temperatures. The boiling-point is  $-90^\circ$ . The molecular weight of the oxide is 44 and its formula  $\text{N}_2\text{O}$ .

Nitrous oxide parts with its oxygen rather more readily than nitric oxide so that it will not only continue to support combustion of brightly burning wood as nitric oxide does, but will even cause a glowing splinter to burst into flame. Briskly burning phosphorous and sulfur will also continue to burn vigorously in

nitrous oxide. In all cases, oxides are formed and nitrogen set free.

Nitrous oxide when breathed produces insensibility, and hence it is used as an anesthetic. The body does not decompose the nitrous oxide in such a way as to utilize the oxygen, so when it is to be breathed for any length of time, it is mixed with the amount of oxygen required to support life. For use as an anesthetic, very pure nitrous oxide is put on the market in the liquid form in strong iron cylinders.

**Nitrogen and Life.**—Compounds of nitrogen are always present in all living organisms. They are especially abundant in the brain, nerves, and muscles, or, in short, in the tissues which seem to be most closely connected with the vital functions. Most organisms are entirely unable to make any use of the great store of free nitrogen in the air, but must get it from ready formed compounds. The plants as a rule get theirs from the nitrates, etc., which are present in the soil, while the animals obtain the compounds directly or indirectly from the plants.

Upon the decay of these organisms a portion of the nitrogen is liberated in the free state. From this it would seem that the supply of available nitrogen compounds must be continually decreasing. However, there are two important natural processes going on which tend to keep up the supply of nitrogen compounds available for plants. The first of these is the formation of nitric oxide during the passage of lightning through the air. The oxide is then transformed into nitric acid by the action of oxygen and water. This combines with the ammonia of the air to form ammonium nitrate which is carried by the rain into the soil. The second process takes place with the aid of certain forms of bacteria. Some forms are free in the soil, but the most efficient live in tubercles on the roots of leguminous plants such as clover, peas, alfalfa, etc. These bacteria have the power to transform the free nitrogen of the air into compounds which are closely related to the albumins, and which may be easily assimilated by the plant. Such plants will grow and produce abundant crops, and yet leave in the soil an increased amount of nitrogen compounds. This, then, is the explanation for the well-known fact that the fertility of certain soils may be restored by growing upon them these leguminous plants. In the older parts of the country,

It is the custom of farmers to raise a crop of such plants on each portion of cultivated land about once in three years. The farmers of the West will doubtless have to adopt this same custom in the course of time, if they continue to remove everything from the land and return nothing to it, and to burn the stalks and straw as so many do at present.

In addition, as has been mentioned, the compounds of ammonia which are obtained in the manufacture of coal gas and coke, as well as the calcium cyanamide and calcium nitrate which are being made from the nitrogen of the air are available as fertilizers. So there seems to be no danger that the earth will lose its fertility because of lack of combined nitrogen.

## CHAPTER XV

### PHOSPHORUS

**General.**—Phosphorus belongs to a group of elements of which nitrogen is the member with the smallest atomic weight. Just as fluorine, the first member of the halogens, has some points of resemblance to chlorine but many of difference, so the nitrogen compounds have at least a formal similarity to those of phosphorus, but show many marked differences. *It might be said that the root of the differences lies in the fact that the more highly oxidized compounds of nitrogen are unstable and tend to go to the less highly oxidized, while just the reverse is the case with phosphorus.* Phosphorus, however, differs radically from nitrogen in that the element itself is extremely active chemically. When exposed to the air even at ordinary temperatures it is slowly oxidized, at the same time emitting light. It was on account of this property that phosphorus received its name, which means light bearer.

**Occurrence.**—Phosphorus does not occur free in nature, but is found widely distributed chiefly in the form of phosphates. The most important naturally occurring phosphate is that of calcium,  $\text{Ca}_3(\text{PO}_4)_2$ , which is found in most soils. It constitutes a large part of the bones and teeth of animals. Great beds of calcium phosphate which have been formed in part at least from the fossil bones of animals are found in Florida and Tunis. Enormous beds, probably the largest in the world, of phosphate rock exist in Utah, Montana, Wyoming, and Idaho. A very partial survey of the field has located 2,500,000,000 tons of rock averaging 70 per cent. calcium phosphate. Another mineral which is closely related to calcium phosphate is apatite,  $\text{Ca}_5\text{F}(\text{PO}_4)_3$ . This is a component of many rocks and is found in large quantities in Canada. The importance of these compounds of phosphorus may be realized when it is known that phosphorus like nitrogen is an absolutely essential component of all living organisms, and

hat soluble compounds of this element must be present in a soil in order that it may be fertile. In nearly all of the older agricultural countries, artificial manures containing phosphoric acid must be applied to the land. The world mines about 5,000,000 tons of phosphate rock per year.

**Preparation of Phosphorus.**—The easiest method of preparing phosphorus involves the heating of a mixture of calcium phosphate, sand (silicon dioxide),  $\text{SiO}_2$ , and carbon to a very high temperature in an electric furnace (Fig. 37). Calcium silicate,  $\text{CaSiO}_3$ , carbon monoxide,  $\text{CO}$ , and phosphorus are formed.

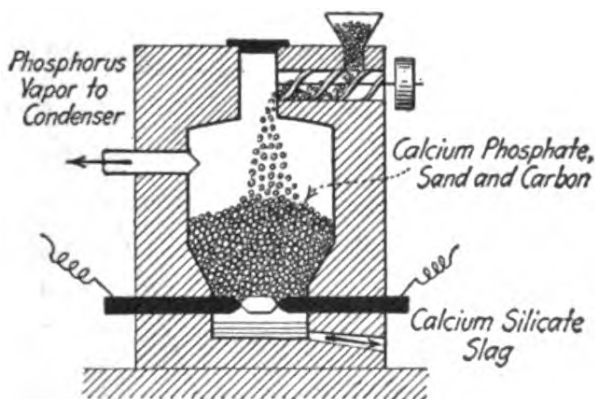


FIG. 37.

The carbon monoxide and phosphorus pass out of the furnace in the gaseous state, the phosphorus being condensed under water. The calcium silicate is liquid at the temperature of the reaction and is drawn off from the furnace from time to time. The whole process may be made continuous by feeding in the reaction mixture as rapidly as it is used up. The equation is:



**The Allotropic Modifications of Phosphorus.**—The element phosphorus exists in two different modifications which are so very unlike that it is hard to believe that they are composed of the same element. One of these is called ordinary, yellow, or sometimes white phosphorus; the other is known as red phosphorus. In addition there is a black variety which is much like the red.

**Ordinary phosphorus** is prepared by the method described above and is a slightly yellowish almost colorless wax-like solid. It melts at  $+44^\circ$  and boils at  $270^\circ$ . It is readily soluble

in carbon disulfide and some other organic solvents, but is nearly insoluble in water, under which it is always preserved. From its solution in carbon disulfide, crystals of phosphorus may be easily obtained.

When exposed to the air, this form of phosphorus is slowly oxidized with the formation of phosphorus trioxide,  $P_4O_6$ , and at the same time shines so that it may easily be seen in the dark. In a limited amount of air, the luminosity will continue until the last detectable trace of oxygen has been used up. The temperature of the phosphorus is but little higher than its surroundings, so a part of the chemical energy of the change must be converted directly into light. The fumes given off have a

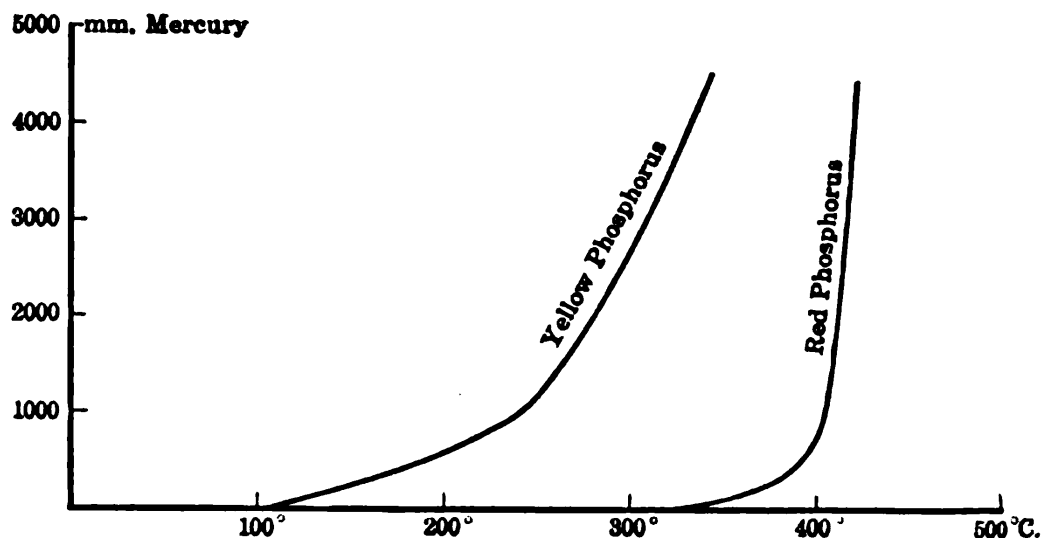


FIG. 38.

strong garlic-like smell and their continual inhalation produces a very serious disease in which the bones of the jaw decay. Matchmakers are particularly liable to this trouble. The element itself is very poisonous, a tenth of a gram being a fatal dose. During the slow oxidation of the phosphorus, a part of the oxygen of the air is changed into ozone. If the temperature of phosphorus exposed to air is gradually raised, the oxidation goes on more and more rapidly until at about 45° it passes into rapid combustion.

The molecular weight of phosphorus, both as vapor and in solution is 124, and, since its atomic weight is 31.04, the formula is  $P_4$ .

**Red phosphorus** is very different from the ordinary form. It is a dull red crystalline powder and may be obtained by heating the yellow variety to 250° in the absence of air. The transformation is catalyzed by iodine so that in the presence of a trace of this substance the transition takes place very rapidly indeed at 200°. Light also hastens the change, and sticks of phosphorus which have been exposed at ordinary temperatures to the action of light are covered with a thin layer of red phosphorus.

Red phosphorus does not melt but passes directly into the vapor which is identical with that of yellow phosphorus, and yields the latter modification when it is rapidly cooled. In fact, it is only by converting the red phosphorus into the vapor and condensing the latter that the change from the red into the other modification can be made.

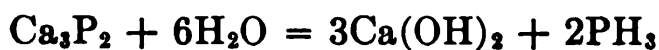
Red phosphorus is not poisonous, is not soluble in carbon disulfide, does not oxidize in the air at ordinary temperatures, nor take fire until heated to about 260°. It is, then, very different from the ordinary phosphorus, and yet the two modifications can be converted the one into the other without any change in weight.

The yellow modification is at all ordinary temperatures unstable with respect to the red. In accord with this is the fact that yellow phosphorus is more soluble than red and has the greater vapor pressure as shown by the curves given in Fig. 36. The vapor pressure curves do not intersect so there is no transition point within the range 100°–400°, but there is a little evidence that a transition point may exist at –77°.

When yellow phosphorus is heated to 200° under a pressure of about 4,000 atmospheres it is changed into a more dense variety which because of its color is called **black phosphorus**. This is chemically much like the red modification.

**Hydrogen Compounds of Phosphorus.**—Hydrogen and phosphorus form three compounds, phosphine,  $\text{PH}_3$ , liquid hydrogen phosphide,  $\text{P}_2\text{H}_4$ , and solid hydrogen phosphide,  $\text{P}_4\text{H}_2$ . Phosphine is similar to ammonia in its formula and is slightly like it in its properties.

Phosphine may be readily prepared by dropping pieces of calcium phosphide,  $\text{Ca}_3\text{P}_2$  (Fig. 39), in water.



The action is very much like that between magnesium nitride and water with the formation of ammonia. The addition of a little acid facilitates the reaction by rapidly dissolving the calcium hydroxide. The phosphine prepared in this way is spontaneously inflammable.

As each bubble of phosphine rises to the surface of the water it catches fire with a little explosion and burns to phosphoric acid

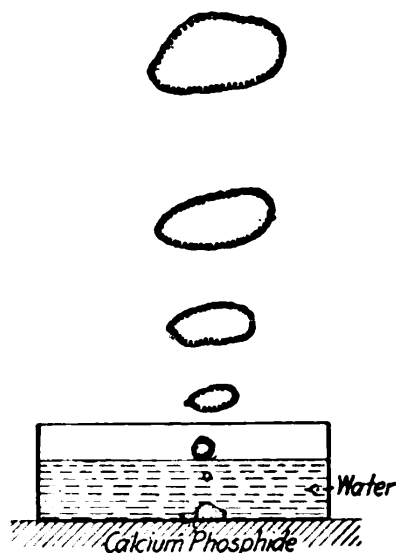


FIG. 39.

which forms a beautiful smoke ring. Pure phosphine is not spontaneously inflammable. The compound prepared as described above contains small quantities of the vapor of the liquid hydrogen phosphide, and it is to this that it owes the property of catching fire on contact with the air.

Calcium phosphide has found application in connection with life buoys to indicate their position at night when they are thrown into the water.

The phosphine may be so far purified from the liquid compound by passing it through a tube surrounded by a freezing mixture that it will not take fire on contact with the air.

Phosphine is a colorless gaseous substance which boils at  $-86^{\circ}$ , smells like decayed fish and is very poisonous. At high temperatures it is decomposed into its elements. It resembles ammonia in its formula and because it combines directly with the hydrohalogen acids to form phosphonium salts. It differs from ammonia in that it is scarcely at all soluble in water and does not form a basic compound with this substance nor does it combine with the oxyacids to form salts.

**Phosphonium Compounds.**—Phosphonium iodide is the most stable of these compounds and is easily formed by bringing together at ordinary temperatures and pressures phosphine and hydrogen iodide,



It forms beautiful large transparent quadratic crystals which sublime at  $62^{\circ}$ . In the vapor state, it is very largely decomposed

into phosphine and the acid, just as ammonium salts are decomposed into ammonia and the acid. It is a powerful reducing agent and finds use as such in the laboratory.

Phosphonium bromide is very similar to the iodide, and is prepared from hydrogen bromide and phosphine at ordinary temperatures and pressures. It sublimes at  $38^{\circ}$ .

Phosphonium chloride cannot be prepared by bringing hydrochloric acid and phosphine together at ordinary temperatures and pressures. At  $-35^{\circ}$  it can be obtained at ordinary pressures, but requires a total pressure of at least 18 atmospheres at  $14^{\circ}$  to produce it or to keep it from decomposing into its components. Phosphonium compounds are decomposed by water into phosphine and the acid. From this we gather that the phosphonium ion,  $\text{PH}_4^+$ , is not stable.

**Liquid Hydrogen Phosphide.**—Liquid hydrogen phosphide boils at  $57^{\circ}$ . The vapor is spontaneously inflammable. Its analysis and molecular weight indicate that the formula is  $\text{P}_2\text{H}_4$ .

**Halogen Compounds of Phosphorus.**—Each of the halogens will combine directly with phosphorus forming fairly stable compounds.

Chlorine, bromine and iodine form trihalides,  $\text{PCl}_3$ , for example, which are all liquids. Fluorine, chlorine and bromine form penta compounds,  $\text{PCl}_5$ , for instance; with the exception of the fluoride which is gaseous, these are solids.

Each of these compounds is decomposed by water with the formation of an oxyacid of phosphorus and the hydroacid of the halogen. It will be recalled that this property was made use of in the preparation of hydriodic and hydrobromic acids. The chlorine compounds are rather more important than the others and will be described in some detail.

**Phosphorus trichloride**,  $\text{PCl}_3$ , is formed by passing chlorine over phosphorus contained in a retort to which is connected a receiver. The combination takes place with the evolution of so much heat that the greater part of the trichloride formed distills over and condenses to a colorless liquid in the receiver. It boils at  $76^{\circ}$  and has a density of 1.6. It reacts with water and other compounds containing oxygen and hydrogen to form phosphorous acid and hydrogen chloride. Because of this it fumes when in contact with moist air.

**Phosphorus pentachloride**,  $\text{PCl}_5$ , is prepared by the action of an excess of chlorine upon the trichloride. It is a pale yellowish-green solid which when heated under atmospheric pressure does not melt, but passes directly into the vapor without going through the liquid state. This is due to the fact that the temperature at which the vapor pressure of the solid is equal to the pressure of the air is lower than its melting-point. We might say that its boiling-point is lower than its freezing-point. When the vapors are cooled they pass directly back to the solid state. That kind of distillation in which the solid passes directly into the vapor and reappears in the solid state upon cooling without the liquid modification coming in as an intermediate step is called sublimation. By heating the pentachloride under pressure, the boiling-point may be so raised that it lies above the melting-point which is  $166^\circ$ . In the vapor state, phosphorus pentachloride,  $\text{PCl}_5$ , is partially decomposed into chlorine and the trichloride.

Phosphorus pentachloride fumes strongly in contact with air and has a very irritating action on the mucous membrane. It rapidly reacts with water, forming phosphoric acid,  $\text{H}_3\text{PO}_4$ , and hydrogen chloride.

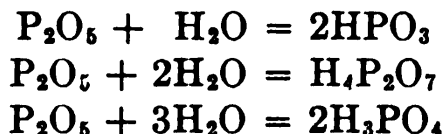
**Oxygen Compounds of Phosphorus.**—The oxides of phosphorus are the tetroxide,  $\text{P}_2\text{O}_4$ , and trioxide,  $\text{P}_2\text{O}_3$ , or  $\text{P}_4\text{O}_6$ , and the pentoxide,  $\text{P}_2\text{O}_5$  or  $\text{P}_4\text{O}_{10}$ . The simpler formulas for the last two oxides are the ones which are the more commonly used for these substances, but the more complicated ones correspond to their molecular weights.

Phosphorus pentoxide is a white powder which is formed when phosphorus burns in dry air. It is exceedingly hygroscopic, and instantly combines with water to form metaphosphoric acid,  $\text{HPO}_3$ . It is the most thorough drying agent known, much better than sulfuric acid and far better than calcium chloride. Owing to its great affinity for water, it will even withdraw the elements of water from compounds containing hydrogen and oxygen. Its use in the preparation of nitric anhydride depends upon this property.

The trioxide is formed when phosphorus burns in a limited supply of air. It differs from the pentoxide in that it has a low melting-point,  $22.5^\circ$ , and boiling-point,  $173^\circ$ , and hence may be easily separated from the higher oxide by distillation. It is

colorless. With cold water it reacts very slowly forming phosphorous acid, and hence is often called phosphorous anhydride.

**Acids of Phosphorus.**—Phosphorus pentoxide is the anhydride of three important acids, metaphosphoric acid,  $\text{HPO}_3$ , pyrophosphoric acid,  $\text{H}_4\text{P}_2\text{O}_7$ , and orthophosphoric acid,  $\text{H}_3\text{PO}_4$ . These are formed by the interaction of varying quantities of water and the anhydride:



In addition to these three acids there are the less important ones, phosphorous acids,  $\text{H}_3\text{PO}_3$ , hypophosphoric acid,  $\text{H}_4\text{P}_2\text{O}_6$ , and hypophosphorous acid,  $\text{H}_3\text{PO}_2$ . The pentoxide is not the anhydride of these last three acids and it will be noticed that the valence of the phosphorus is 3, 4 and 1 respectively.

**Orthophosphoric acid** is of greater importance than any other acid of phosphorus and is always in mind when phosphoric acid is mentioned without qualification. It may be prepared as indicated above, or obtained from its salts by the second general method for the preparation of acids. The first general method is not available since the acid cannot be distilled. It is most conveniently made in pure state by oxidizing ordinary phosphorus with dilute nitric acid, nitric oxide being formed at the same time. By concentrating the solution, the excess of nitric acid is driven off. The orthophosphoric acid obtained in this way is a thick viscous liquid which crystallizes slowly and with difficulty. The melting-point of the pure acid is  $41^\circ$ .

Its solution in water reddens litmus and has a pure agreeable acid taste. It is not very strongly dissociated. A solution of one gram equivalent of phosphoric acid in a liter of water contains only about one-fourteenth as much hydrogen as ion as a hydrochloric acid solution of the same concentration.

Orthophosphoric acid is a tribasic acid as is indicated by its formula,  $\text{H}_3\text{PO}_4$ . It forms three series of salts according as one, two, or all three of the atomic weights of hydrogen per mole are replaced by metals. We have then normal salts and two kinds of acid salts. These latter are distinguished by using Greek numerals to show how many atomic weights of metal are present.

Thus we have normal sodium phosphate,  $\text{Na}_3\text{PO}_4$ , which is often called trisodium phosphate; disodium phosphate,  $\text{Na}_2\text{HPO}_4$ ; and monosodium phosphate,  $\text{NaH}_2\text{PO}_4$ . The names tertiary, secondary and primary are also used to designate these salts. Solutions of the mono salt are slightly acid in reaction while those of the disodium salt are faintly alkaline, and of the tri- exceedingly so. These phenomena are connected with the fact that phosphoric acid is a weak acid and also polybasic. Like all other polybasic acids, it dissociates one atomic weight of hydrogen more strongly than the rest. The dissociation  $\text{H}_3\text{PO}_4 = \text{H}^+ + \text{H}_2\text{PO}_4^-$  takes place to a fair degree, while that of  $\text{H}_2\text{PO}_4^- = \text{H}^+ + \text{HPO}_4^{--}$  is slight, and  $\text{HPO}_4^{--}$  scarcely breaks down at all into  $\text{H}^+$  and  $\text{PO}_4^{---}$ . Because of the weakly acid character of the ions  $\text{HPO}_4^{--}$  and  $\text{H}_2\text{PO}_4^-$ , the trisodium salt is almost completely hydrolyzed into the disodium salt and sodium hydroxide, and the disodium phosphate is also slightly affected.

The phosphates which occur in nature are the normal salts and the principal one is that of calcium,  $\text{Ca}_3(\text{PO}_4)_2$ . This salt is almost universally present in the soil. It is, however, very slightly soluble so that it is only slowly available as a source of phosphorus compounds for plants. Monocalcium phosphate,  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ , is easily soluble and makes an excellent fertilizer. It is known in commerce as "superphosphate" and is prepared by treating calcium phosphate with dilute sulfuric acid from the lead chambers. So extensive is the use of phosphate fertilizers that the larger part of the sulfuric acid made is used in their manufacture.

**Pyrophosphoric Acid.**—When orthophosphoric acid is carefully heated to about  $250^\circ$ , it loses water and is changed into pyrophosphoric acid,  $\text{H}_4\text{P}_2\text{O}_7$ ,



When dissolved in water, it gradually reacts with the latter forming the ortho acid. The formula indicates that it is tetrabasic, and it forms four series of salts,  $\text{NaH}_3\text{P}_2\text{O}_7$ ,  $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ ,  $\text{Na}_3\text{HP}_2\text{O}_7$ , and  $\text{Na}_4\text{P}_2\text{O}_7$ . Of these the second and fourth are the best known.

**Metaphosphoric Acid.**—Metaphosphoric acid,  $\text{HPO}_3$ , may be obtained by heating orthophosphoric acid to a higher tempera-

ture than that required for the preparation of pyrophosphoric acid, or by adding the proper amount of water to the pentoxide.

Metaphosphoric acid melts at a rather high temperature and solidifies to a wax-like mass on cooling. It is put on the market in the form of transparent sticks and is known in commerce as glacial phosphoric acid. These sticks are hard and glass-like because they contain a little sodium metaphosphate. At high temperatures it passes into vapor, and in this state has the formula  $(\text{HPO}_3)_2$  as is shown by its molecular weight.

At room temperatures, a solution of metaphosphoric acid is changed rather rapidly into pyrophosphoric acid and the latter then more slowly into the ortho acid.

The sodium salt of metaphosphoric acid is formed by heating monosodium orthophosphate to a high temperature,



or by heating sodium ammonium phosphate,  $\text{NaNH}_4\text{HPO}_4$ ,



Sodium metaphosphate fuses to a clear glass-like mass and in the fused state is able to dissolve most of the oxides of the metals, receiving from them in many cases, colors characteristic of the metals. This property is made use of in blowpipe analysis.

**Phosphorous Acid.**—Phosphorous acid,  $\text{H}_3\text{PO}_3$ , is formed by the action of cold water upon phosphorus trioxide,  $\text{P}_4\text{O}_6$ , or of water upon the tri-chloride, bromide, or iodide of phosphorus. Its formula indicates that it is a tribasic acid, but it will form only two series of salts,  $\text{NaH}_2\text{PO}_3$  and  $\text{Na}_2\text{HPO}_3$ . This property is probably due to an extreme case of the difference in the degree of dissociation of the hydrogens of a polybasic acid, to which attention was called under phosphoric acid.

Phosphorous acid is a crystalline solid melting at  $70^\circ$ . When heated strongly, it decomposes into phosphine, metaphosphoric acid, and water. It is a powerful reducing agent, being oxidized to phosphoric acid.

**Phosphorus Sulfides.**—By heating red phosphorus and sulfur together in the proper proportions in the absence of air, a rapid reaction takes place, and according to the relative proportions of the substances, the sulfides  $\text{P}_4\text{S}_3$ ,  $\text{P}_2\text{S}_3$ ,  $\text{P}_3\text{S}_6$ , and  $\text{P}_2\text{S}_5$  are formed.

Of these sulfides,  $P_4S_3$  is the most important, because of its use in matches. It does not take fire spontaneously, but does so when gently heated. Red phosphorus is used because the reaction is too violent with yellow.

With water the sulfides react to form hydrogen sulfide and the acids of phosphorus.

**Applications of Phosphorus.**—By far the greater part of the phosphorus made is used in the manufacture of matches. These may be divided into two classes, those which will strike anywhere, and those which will ignite only when rubbed on a specially prepared surface. The first kind are made by dipping the sticks into melted paraffin, and then into a paste containing glue, powdered glass, iron oxide, lead oxide, and phosphorus sesquisulfide,  $P_4S_3$ . The phosphorus sulfide is enclosed within the mass and so protected from the air. Upon striking the match the friction raises the temperature, at the point of contact, above the kindling point of the phosphorus sulfide. The whole very combustible mixture in the head then burns and sets fire to the wood. These matches are so easily ignited that they are liable to produce accidental fires. This type of match was formerly made with free phosphorus and was highly poisonous, but the kind containing phosphorus sulfide is practically non-poisonous.

The second kind is the safety match which lights on the box. The head of this match may contain potassium chlorate and dichromate, sulfur, manganese dioxide, iron oxide, powdered glass, glue, and gum arabic, but no phosphorus. The striking surface on the box is composed of a mixture of red phosphorus, antimony trisulfide, dextrine, and lampblack. Safety matches may sometimes be ignited by friction on a non-conducting surface such as that of glass. Since these matches contain no ordinary phosphorus they are relatively non-poisonous and can be manufactured without injury to the workmen. For the reason that it is practically impossible that they should be ignited accidentally, this form of match is much superior to the other for domestic purposes. In the laboratory red phosphorus is used wherever possible, because it is more moderate in its action and less dangerous than the yellow.

## CHAPTER XVI

### CARBON

**General.**—Carbon belongs to a family of elements, which in their highest state of oxidation are tetravalent; the other members of the family are silicon, germanium, tin, and lead. Carbon and silicon are non-metallic elements, while the others are metals and will be discussed later. The compounds of carbon are exceedingly varied, more than a hundred and fifty thousand of them being known. In fact, the chemistry of carbon is so complex that it is considered a separate branch, and is called organic chemistry. It received this name because all living organisms contain carbon compounds, and it was for a long time supposed that most of these substances could be produced only by the life processes of such organisms. At the present day so many of these compounds have been synthesized in the laboratory that we are now of the opinion that it is possible to prepare any carbon compound artificially.

The great importance of the compounds of carbon may be realized when we consider that nearly all of our foods, and most of our medicines, consist essentially of these substances, and that the principal source of the energy which we use in our various industries is the carbon in coal, gas, oil, etc.

**Occurrence.**—Carbon occurs free in nature in two distinct allotropic crystalline modifications, which are known as diamond and graphite. A third form of elementary carbon, known as amorphous carbon, or charcoal, may be obtained by heating organic substances, such as wood, sugar, etc., to a high temperature in the absence of air. Many persons consider that amorphous carbon is present in coal and so would say that this form of carbon occurs in nature. In combination, carbon is found as an essential constituent of all living organisms; as carbon dioxide in the air and water; as calcium carbonate in the great beds of limestone; as very complex compounds chiefly in combination

with hydrogen in coal and oil; and as methane,  $\text{CH}_4$ , in natural gas.

**Diamond.**—As is well known, diamond is a clear colorless substance which crystallizes in octahedrons and is exceedingly hard. Because of these properties, its rarity and the fact that it has a very brilliant luster, diamond has long been valued highly as a gem. The principal localities in which diamonds are found at the present day are Brazil and South Africa. In Brazil, they are obtained from alluvial deposits, while in South Africa they occur within and in the immediate vicinity of old volcanic chimneys. The diamonds have apparently been formed from carbon under great pressure, at the high temperature of the lava. They are usually small, very rarely weighing more than a few grams; but one, the Cullinan diamond, was found in 1905 at Premier mine in Transvaal which weighed 620 grm., or 3,024 carats, or 1.37 lb., and even then the stone was evidently merely a fragment of a much larger one.

Very small diamonds have been prepared artificially by Moissan. He placed charcoal made from sugar in cast-iron heated to a very high temperature in an electric furnace and then cooled the iron as rapidly as possible. Under these conditions a rigid shell of solid cast-iron was quickly formed around the outside of the mass, while the interior still remained molten. Now cast-iron upon solidification increases in volume, so that, as the interior gradually froze, great pressure was produced. Under these conditions the carbon was simultaneously exposed to very high temperature and pressure, and a small portion of it crystallized as minute diamonds. Because of its extreme hardness it is used for cutting and writing on glass and many other purposes where such a property is required. The density of diamond, 3.5–3.6, is greater than that of the other forms of carbon. When diamonds are heated in the air, or oxygen, they burn to carbon dioxide. Toward most chemical reagents it is very indifferent.

**Graphite.**—Graphite is the second crystalline modification of carbon. It occurs in many localities, chiefly Austria and Ceylon, in rather poorly formed rhombohedral crystals. It is black in color, non-transparent, so soft that it may be readily scratched with the finger nail, and leaves a black streak on paper, has a density of 2.25. and so differs radically in its properties from

diamond. It is prepared artificially on a large scale by heating petroleum coke, anthracite coal, or any other nearly pure form of carbon, to a very high temperature in the electric furnace (Fig. 40). Graphite is highly resistant to chemical action, but rather less so than diamond. When heated in the air, or oxygen, it slowly burns to carbon dioxide. When heated alone it undergoes no change until the highest temperature of the electric arc is reached, when it passes slowly into vapor without melting. Because of its infusibility, graphite when mixed with a small portion of clay to act as a binder, is used in making crucibles which have to stand

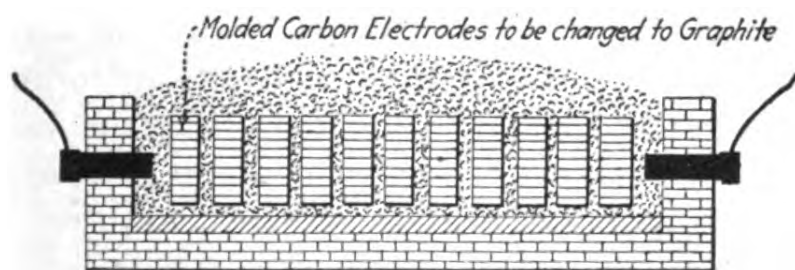


FIG. 40.

high temperatures. Because of these same properties and the further fact that it is a good conductor of electricity, graphite is extensively used at present for making electrodes for use in electric furnaces and in the electrolytic industries. Crystals of graphite very easily break up into fine scales which slip over one another with but little friction. On this account it is often used as a lubricant. Finely ground graphite mixed with clay and slightly baked, constitutes the "lead" of our lead pencils. The more clay the harder the pencil.

**Amorphous Carbon.**—As has been mentioned above, amorphous carbon is prepared by heating certain carbon compounds to a high temperature in the absence of air. A rather large number of different forms are distinguished according to their state of division and the substances from which they were formed. We have, for example, charcoal of various kinds, soot or lamp black, and coke. The density, hardness and electrical conductivity of all forms of amorphous carbon increase with the temperature to which they are heated. At the highest temperatures of the electric furnace, the various forms of amorphous carbon are transformed into graphite. Like graphite, amorphous carbon

is infusible. It is, however, much more easily combustible than graphite.

**Soot** is a comparatively pure form of finely divided carbon and is formed by the combustion of various carbon and hydrogen compounds with an insufficient supply of air. It is very soft, intensely black, has a small density, is easily combustible, and is a good non-conductor of heat or electricity. It finds application as a pigment in printer's ink, paint, etc., under the name of lampblack.

**Charcoal.**—The most common form of charcoal is that prepared by heating wood to fairly a high temperature in cast iron retorts. In addition to the charcoal, methyl or wood alcohol,  $\text{CH}_3\text{OH}$ , acetic acid,  $\text{CH}_3\text{COOH}$ , and creosote are formed and are condensed, separated and sold for more than the value of the charcoal. Bone charcoal or bone-black as it is called, is made by carbonizing bones in retorts. At the same time a valuable by-product known as bone oil is produced. All solid substances seem to have a tendency to increase, right at their surface, the concentration of any gaseous substance with which they may be in contact. This property is called adsorption. It is shown strongly by all forms of charcoal, especially by those such as bone and cocoanut shell charcoal which have per unit weight very large surfaces owing to the fineness of the pores of the materials from which they were made. The higher the molecular weight and boiling point of the gas and the lower the temperature, the greater is the adsorption.

When cooled to the temperature of liquid air, cocoanut shell charcoal will adsorb very completely all gases except hydrogen, helium and neon. One of the most convenient ways for producing a high vacuum is to seal a bulb containing cocoanut charcoal to the vessel to be exhausted and then cool the bulb with liquid air. In a short time, the air in the vessel will be so completely taken up by the charcoal that a very high vacuum will be produced.

When charcoal is added to solutions it adsorbs nearly every substance present. This is more pronounced with bone-black than other charcoals for the reason given above. Here again, the adsorption is more complete the higher the molecular weight of the substance affected, and since coloring matters are usually very complex, they are adsorbed to a greater extent than most

other substances. Crude sugar contains a coloring matter which is removed in refining by boiling a solution of the sugar with bone-charcoal. Some of the sugar is adsorbed, but not enough to make a serious loss. Charcoal is a catalyzer for many reactions, particularly between gases. Here again we are dealing with a surface phenomenon, and the charcoals prepared from the more finely cellular substances are the more active.

**Coal** may be considered natural charcoal, and has probably been formed by the partial decomposition of vegetable matter under water. Various varieties of coal are distinguished, such as anthracite, semi-anthracite, bituminous, and lignite. These differ rather widely in the relative proportions of carbon, hydrogen, nitrogen, oxygen, sulfur, and mineral matters which they contain, the anthracite being the nearest pure carbon, and the others decreasing in purity in the order named. The world's production of coal is about 1,300 million tons and that of the United States about 500 million tons each year.

**Coke** is formed by heating bituminous coal with the exclusion of air until practically all the volatile matter has been distilled off. The gases given off are rich in compounds of carbon and hydrogen, and are very valuable for fuel and illuminating purposes. In addition, they contain many useful products, such as ammonia, benzene,  $C_6H_6$ , coal tar, etc. Coke is largely used as a fuel in blast furnaces and many other metallurgical operations, since it produces a very high temperature, burns without smoke and contains a relatively small amount of sulfur.

**Relation Between the Allotropic Modifications.**—Although the various modifications of carbon differ so radically in their properties they are really composed of the one element carbon, and contain nothing else, as is shown by the following argument. When equal weights of pure diamond, graphite, or amorphous carbon are burned in oxygen, equal weights of carbon dioxide are produced in each case, and nothing besides carbon dioxide is formed in any case. The heat of combustion of the various modifications is different so that in this, as in other cases, the allotropic modifications differ in their energy content. Because of the non-volatility and insolubility of carbon, it is impossible to determine its molecular weight. Its atomic weight, however, is 12.005.

**Oxygen Compounds.**—Carbon forms two well known oxides, the monoxide  $\text{CO}$ , and the dioxide  $\text{CO}_2$ . The second of these compounds is by far the more important.

**Carbon Dioxide.**—Carbon dioxide,  $\text{CO}_2$ , is a gaseous substance whose molecular weight is 44. It is colorless, has a very feeble taste and odor, its critical temperature is  $31^\circ$ , and its critical pressure is 73 atmospheres.

Liquid carbon dioxide is a common article of commerce. It is sold in very strong cylinders. At a temperature of  $20^\circ$  its vapor pressure is 58.5 atm. or 860 lb. to the square inch, so it may be easily seen that the cylinder should be well constructed and handled with care. The principal use for this carbon dioxide is in the manufacture of soda water and other carbonated beverages. The boiling-point, or rather subliming-point of carbon dioxide is  $-78.2^\circ$ ; the freezing-point is considerably higher than this  $-57^\circ$ ; so that at ordinary pressures liquid carbon dioxide cannot exist in open vessels. Liquid carbon dioxide is a colorless, very mobile substance, which is but slightly soluble in water. It is not a conductor of electricity, does not act as a solvent toward most substances, and does not redden litmus paper; in short, it does not present any striking chemical properties.

Solid carbon dioxide may be formed by allowing the liquid modification to flow out from the cylinder at any temperature below the critical temperature of the liquid. As soon as the liquid comes in contact with the air, the greater portion of it is at once turned into vapor. The heat necessary for this transformation is absorbed largely from the carbon dioxide itself, and so far cools a portion of this that it assumes the solid state, although its temperature in this condition is  $-78.2^\circ$ .

The solid carbon dioxide is a white snow-like substance which is very convenient for use as a cooling agent, since we can so easily get with it the definite temperature of  $-78.2^\circ$ . In order to secure better thermal contact with the substance to be cooled, it is commonly mixed with ether. By diminishing the pressure upon the carbon dioxide, temperatures lower than  $-78.2^\circ$  may be obtained. In this way by causing it to evaporate in a vacuum, a temperature of  $-100^\circ$  may be reached.

Carbon dioxide occurs in nature in very large quantities. The air contains three to four parts of this substance to ten thousand

parts by volume. It escapes in great volumes from volcanoes, mineral wells and springs, and at various places on the earth it issues in an almost pure state from fissures. It is formed during the breathing of animals and in the fermentation and decay of organic substances. It may be prepared by burning carbon or any carbonaceous material in an excess of oxygen or of air; or by heating limestone, calcium carbonate,  $\text{CaCO}_3$ , in lime kilns where it breaks down into calcium oxide,  $\text{CaO}$ , and carbon dioxide,  $\text{CO}_2$ ;



or by the action of an acid upon a carbonate. The carbon dioxide which is put on the market in the liquid form is very largely obtained from lime kilns and from the fermentation vats of the breweries. The ordinary laboratory method for its preparation is to place some pieces of marble, which is a very pure form of calcium carbonate, in a flask and allow hydrochloric acid to run slowly upon them. Under these conditions the carbon dioxide is given off in a steady stream,



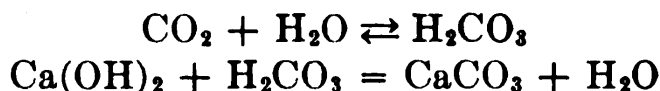
Being heavier than air and not very soluble in water, it may be collected either by the displacement of air or over water. Carbon dioxide is neither a supporter of combustion nor of animal life. Air containing 4 per cent. of carbon dioxide will extinguish a candle flame, but will support respiration for a short time. Since carbon dioxide is heavier than air and is being gradually given off by the earth, it often accumulates in old wells, cellars, cisterns, etc., in quantities sufficient to render it dangerous to persons entering such places. The presence of carbon dioxide in dangerous quantities may be easily detected by the lowering of a lighted lantern. If the flame is extinguished no one should enter until the excavation has been thoroughly ventilated.

It dissolves in its own volume of water at ordinary temperatures and the solubility follows Henry's law.

The solution has a feebly acid reaction and contains the very unstable substance, carbonic acid,  $\text{H}_2\text{CO}_3$ . This is a very weak dibasic acid which forms two series of salts, the normal and the acid carbonates. Because of the weakness of carbonic acid, the easily soluble normal salts are rather strongly hydrolyzed and

are alkaline in reaction; and the so-called acid salts are almost neutral in their reaction. The most abundant naturally occurring carbonate is that of calcium,  $\text{CaCO}_3$ . Sodium carbonate,  $\text{Na}_2\text{CO}_3$ , is manufactured in enormous quantities from sodium chloride, and is a very important chemical. Sodium, potassium and ammonium carbonates are soluble in water. Most of the other carbonates are not soluble.

When an acid is poured on a carbonate, the carbonic acid formed decomposes at once with a brisk effervescence due to the escape of carbon dioxide. Such an effervescence suggests a carbonate but does not prove its presence because a few other salts, sulfites and sulfides, for example, will also effervesce. The best test for carbon dioxide is the formation of a white precipitate of calcium carbonate when it is brought in contact with lime water, which is a solution of calcium hydroxide in water. The carbon dioxide is first dissolved by the water forming carbonic acid, which then reacts with the calcium hydroxide for the formation of water and the difficultly soluble calcium carbonate,



Because of the fact that carbon dioxide will combine with water for the formation of carbonic acid, it is often called carbonic anhydride.

**Circulation of Carbon.**—During the breathing of animals oxygen is taken up from the air in the lungs forming an unstable compound with the hemoglobin of the blood. It is then carried to all parts of the body and gradually oxidizes the complex compounds contained therein, forming carbon dioxide as one of the products; this is carried by the blood to the lungs and there given up to the air and expired. In the dark practically this same process takes place in plants, but in the light those plants which contain green coloring matter in their leaves are able to bring about the reverse change, partially breaking up the carbon dioxide absorbed from the air, liberating a part of its oxygen in the free state and combining the residue with water for the formation of complex compounds of which the sugars, starches, and celluloses are prominent examples. These compounds are food for plants as well as for all animals,

which live directly or indirectly upon them. This decomposition of carbon dioxide and the building up of complex compounds from it takes place only under the simultaneous influence of chlorophyll, the green coloring matter of plants, and of light. It is accompanied by the absorption of a great amount of energy which is obtained from the light of the sun. The energy so absorbed is given out once more when these complex compounds burn, decay, or oxidize in the bodies of animals; and so the ultimate source of the energy of animals and of all engines, which are driven by the burning of wood and other vegetable products, is the light of the sun. Coal has been formed by the partial decomposition of vegetable organisms, and the energy obtained from it was originally absorbed by these organisms from the light of the sun; so the steam engine of to-day is really driven by the energy of the sunlight of thousands of years ago.

By this cycle of changes, carbon dioxide is successively taken up from and given back to the air, and thus there is in nature a sort of circulation of carbon. The energy, however, accompanying these transformations apparently does not move in any such cycle; that given out during the decomposition of the complex compounds is not available for the re-formation of these substances, and this change can take place only with the influx of a fresh supply of energy from the sun. We are to think of the energy relationships in the following way: A stream of energy comes to the earth in the sunlight; a very small part of this is absorbed by the green plants and stored as chemical energy in the form of complex carbon compounds, which are available for use as foods, or combustibles, and so furnish us with the greater part of the energy which we employ. The other sources of energy which man employs, water power and the wind, are really dependent upon the sun, so that we owe practically all of our stores of available energy to this body.

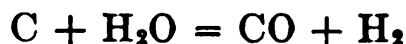
**Photochemical Action.**—Red and yellow light rays are practically the only ones which have any influence on the reactions which take place in plants; while in the photochemical changes in photographic plate, the red rays are almost inactive and blue, green and violet produce most of the effect. From these and similar instances, it follows that every kind of light can produce some kind of chemical change.

**Carbon Monoxide.**—Carbon monoxide is a gaseous substance which is formed when coal is burned in a limited supply of air. It may also be prepared by the action of carbon at a high temperature upon carbon dioxide. The carbon monoxide burns in the air with a pale blue flame, and it is the burning of this substance which produces the blue flames that are so commonly seen at the top of a hard coal fire. The chemical changes taking place in such a fire are mainly as follows: When the air first comes in contact with a hot carbon at the bottom of a firebox, carbon dioxide is formed, which, passing up through the body of the coal, is reduced to carbon monoxide; this burns when it comes in contact with the air at the surface of the fire. The equations for the reactions are as follows,



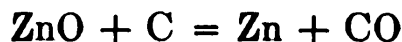
These reactions take place on a large scale in the manufacture of "producer gas" for fuel and power purposes, see p. 250, and also in the iron blast furnace.

When steam is passed over highly heated carbon, carbon monoxide and hydrogen are produced as shown in the equation



This is one of the reactions which takes place in the technically important process for making what is known as water gas. This will be discussed in some detail later, see p. 250.

Carbon is an excellent reducing agent and is much employed for this purpose in the extraction of metals from their oxides. When this change takes place at a high temperature, as is usually the case, carbon monoxide is formed. The equation for the reduction of zinc oxide is

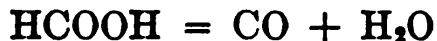


Carbon monoxide is often prepared by heating oxalic acid, a white crystalline substance, whose formula is  $\text{H}_2\text{C}_2\text{O}_4$ , with sulfuric acid. Under these conditions the oxalic acid decomposes into carbon dioxide, carbon monoxide and water,



The carbon dioxide is removed by passing the mixture of gases through a strong solution of sodium hydroxide. Formic acid

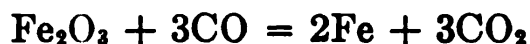
Heated with sulfuric acid breaks down into water and carbon monoxide,



In this reaction and that of oxalic acid the sulfuric acid apparently does nothing except take up the water formed.

**Properties.**—Carbon monoxide is a colorless, tasteless gas with a very faint, peculiar odor, very slightly soluble in water. Its molecular weight 28, critical temperature  $-140^\circ$  boiling point  $-190^\circ$  are nearly the same as those for nitrogen. Carbon monoxide will combine directly with oxygen, chlorine, and many other substances. With oxygen, carbon dioxide is formed with the evolution of much heat, making it an excellent fuel. It combines with chlorine forming the substance,  $\text{COCl}_2$ , carbonyl chloride or phosgene. This combination takes place when carbon monoxide and chlorine are exposed to sunlight, or when a mixture of the two gases is passed over animal charcoal which acts as a catalyzer.

Carbon monoxide is a powerful reducing agent. The reduction of iron oxide to metallic iron by this gas takes place on an enormous scale in the blast furnace. The reaction may be represented by the following equation:



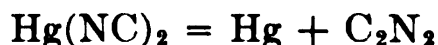
Carbon monoxide is extremely poisonous. This is connected with the fact that it will combine with the hemoglobin of the blood to form a very stable compound which is unable to take up the oxygen of the air. So poisonous is carbon monoxide that 700 c.c. of the gaseous substance will be sufficient to kill an average man.

**Carbon Disulfide.**—When charcoal is heated to a rather high temperature in the vapor of sulfur, the elements combine forming an easily volatile liquid substance, called carbon disulfide,  $\text{CS}_2$ . This substance is now manufactured on a large scale in electric furnaces (Fig. 41). It is a colorless liquid whose boiling-point is  $46^\circ$ . It has a very high index of refraction for light. When perfectly pure it has a pleasant ethereal odor; the commercial article, however, contains impurities which gives it a very disagreeable smell. It is an excellent solvent for sulfur, iodine, phosphorus, rubber, resins, and fats and hence finds extensive use

in the arts and manufactures. A mixture of carbon disulfide vapor and air is violently explosive and is remarkable for the fact that ignition takes place at temperatures as low as  $260^{\circ}$ . On this account even greater care must be taken in handling this substance than is used with gasoline.

**Nitrogen Compounds of Carbon.**—At the very high temperature of the electric arc, carbon and nitrogen will combine directly

with the formation of a gaseous compound, **cyanogen**,  $C_2N_2$ . This substance may also be obtained by heating mercuric cyanide,  $Hg(NC)_2$ . This breaks down into metallic mercury and cyanogen, as shown in the equation,



Cyanogen is a colorless gas, having a peculiar pungent odor resembling that of peach kernels; it is exceedingly poisonous and burns in the air with a characteristic red-violet flame, forming carbon dioxide and nitrogen. Its stability at high temperature is due to its being formed from the elements with the absorption of heat.

Chemically, cyanogen resembles the halogens. It forms a series of salts called cyanides, which are similar to the

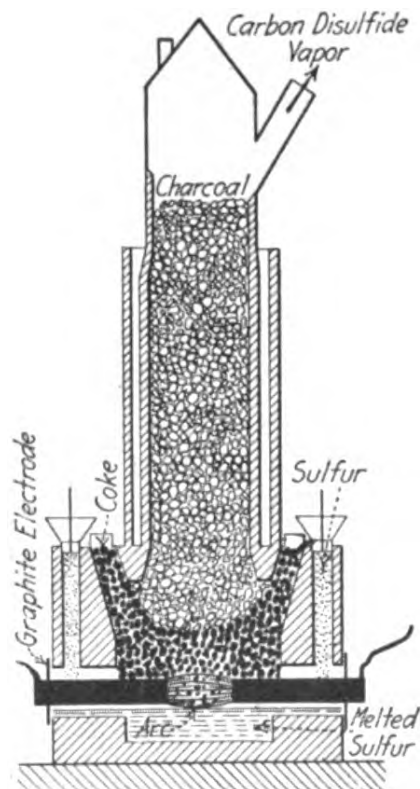


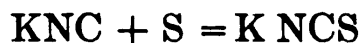
FIG. 41.

chlorides, but contain the group NC, instead of chlorine. Silver cyanide, for example, is a difficultly soluble white substance, which is very much like silver chloride in its general properties. From these salts, **hydrocyanic acid** or prussic acid, HNC, may be easily obtained by the addition of a less volatile acid and distilling. It is a colorless liquid which boils at  $27^{\circ}$  and has a very strong odor like that of peach pits. It is one of the weakest acids. On this account, the soluble cyanides react strongly alkaline when in solution in water, owing to hydrolysis. Hydrocyanic acid and the cyanides are extremely poisonous substances. The poisonous effect of the peach pits is due to hydrocyanic acid formed by the action of water upon a substance called

mygdalin which is in the pit. Not only is hydrocyanic acid a poison toward animals, but it will also stop or "poison" the action of many catalyzers, and it is thought that perhaps the poisonous action of this substance on animals is due to its stopping the catalytic processes which are going on within them.

**Cyanates.**—Cyanides are good reducing agents, and when oxidized often form compounds called cyanates, potassium cyanate,  $\text{KNC O}$ , for example, is formed by cautiously oxidizing potassium cyanide,  $\text{KNC}$ . Cyanic acid, corresponding to these cyanates is very unstable. It is a colorless liquid with a strong smell resembling that of acetic acid.

**Thiocyanates.**—When a cyanide is heated with sulfur, the two substances combine to form a thiocyanate. These correspond to the cyanates. The formation of potassium thiocyanate,  $\text{KNCS}$ , is shown in the following equation,



The thiocyanates are used as reagents for detecting the ferric salts with which they give an intense red coloration.

**The Hydrocarbons.**—Several hundred compounds of carbon and hydrogen have been described. For purposes of classification and as an aid in getting a comprehensive view of their relations, they have been divided into several series according to the composition and general properties of the substances. The principal series is that known as the Marsh Gas or Paraffin series, and the simplest member of this is marsh gas or methane. This series is distinguished by the fact that in all the compounds belonging to it carbon has a valence of 4—the highest valence which it is capable of taking on. For this reason, the members of this series are sometimes called the saturated hydrocarbons. Figure 42 gives the names and formulas, and indicates the melting- and boiling-points of some of the more important of the lower members of the normal paraffins.

An inspection of this figure will show that the boiling- and melting-points of these hydrocarbons increase as they become more complex. It will be noticed, too, that the formula for each succeeding member of the series differs from that of the one which just precedes it by  $\text{CH}_2$ . A series of carbon compounds which are related to one another in this way is called a **homologous**

**series.** The members of such a series have similar properties which gradually change with the composition of the compound. The change in the boiling-points of the compounds shown in the figure is an illustration of this. Most of these hydrocarbons occur in nature in large quantities, the majority of them being found in crude petroleum, while methane and ethane are present in natural gas.

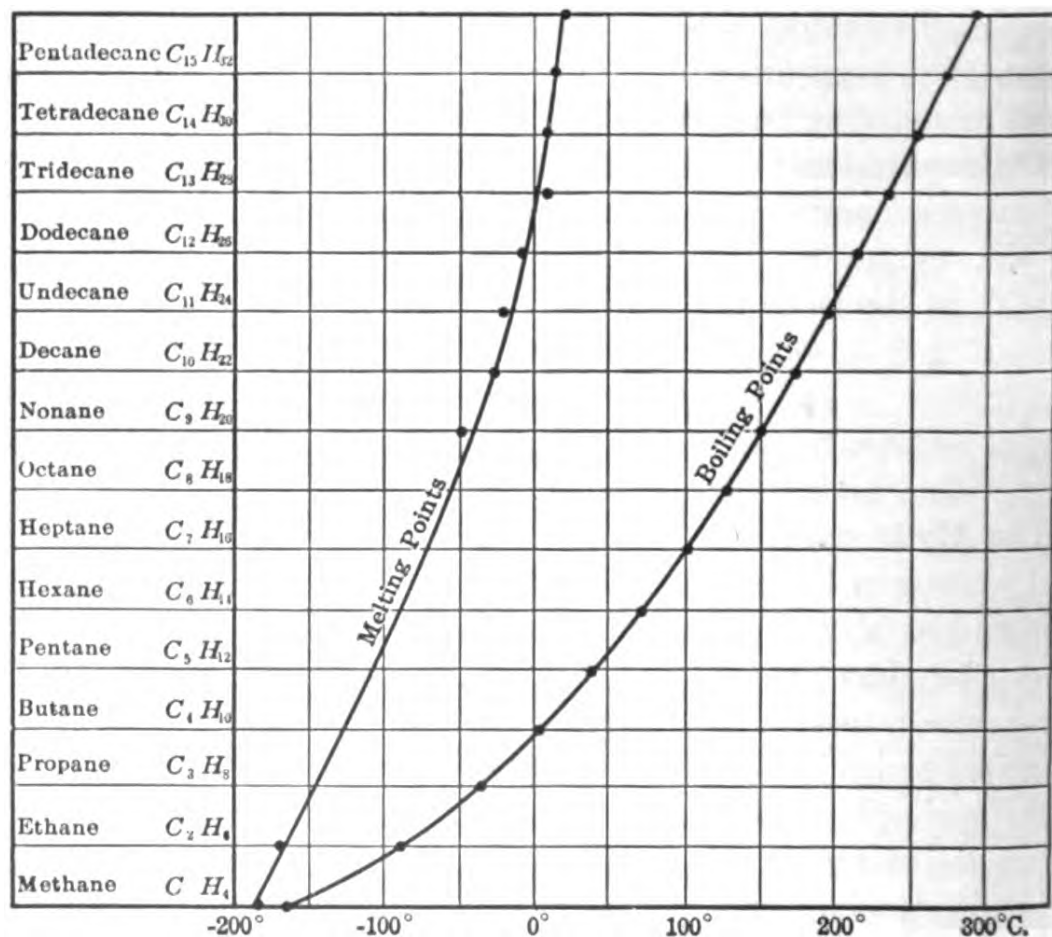


FIG. 42.

**Crude Petroleum.**—Crude petroleum or “oil” is found in many places in the United States, in Ontario, in Baku on the Caspian Sea, in Roumania, in India, and in Japan. This oil is a mixture of a great many substances, but principally of hydrocarbons, and usually consists very largely of the hydrocarbons of the marsh gas series. In oil refining, for commercial purposes, no attempt is made to prepare pure substances from the oil, but the more volatile portions are distilled off and separated into fractions according to their density and adaptability for particular

purposes. The following table gives the name, approximate components, density, and uses for some of the more common products.

SOME COMMERCIAL PETROLEUM PRODUCTS

Trade name	Chief constituent	Density	Use
Rhigoline.....	Pentane.....	0.6222	Solvent; automobiles.
Benzine.....	Hexane.....	0.6511	Solvent; automobiles.
Gasoline.....	Heptane.....	0.722-0.737	Solvent; automobiles.
Naphtha.....	Octane.....	0.745-0.824	Traction and stationary engines.
Kerosene.....	Nonane, decane, etc...	0.791-0.824	Illuminating; fuel; and stationary engines.

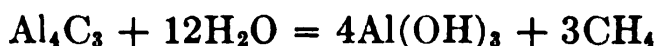
The residue left after removing these substances is then distilled in a current of steam. Some of the higher boiling products which come over under these conditions are used for lubricating oils, but must first be purified from the solid members of the series by cooling to a low temperature and filtering with the aid of filter presses. The solid substances so secured constitute what is known as **paraffin**, while the low melting product, which is salve-like at ordinary temperatures, is called **vaseline**. The final residue left in the retort is used as asphalt. Natural asphalt is a mixture of hydrocarbons which occurs in nature. Just how these hydrocarbons are formed in nature is not known, but they have probably been produced, in most cases at any rate, by the partial decomposition of animal and vegetable organisms, although it is possible that they may have resulted from the action of water upon carbides, compounds of carbon with metals.

Most of the hydrocarbons are rather indifferent chemically. They are not acid like hydrogen chloride nor basic like ammonia. They of course burn in oxygen, forming carbon dioxide and water, and react with chlorine or bromine to form compounds. When heated to a very high temperature they all show a tendency to break down into hydrogen, carbon and simpler hydrocarbons containing a relatively smaller amount of carbon. The process

is technically known as "cracking" and is now used on a large scale to increase the yield of gasoline.

**Methane.**—Methane or marsh gas,  $\text{CH}_4$ , is the first member of the paraffin series. It is the principal constituent of natural gas. It is formed during the decay of vegetable matter in the bottom of ponds and marshes, and to this fact it owes its name, marsh gas. It is found in considerable quantities in coal, and since its mixture with air is explosive, it is one of the causes of the disastrous coal mine explosions. When found in mines it is often called "fire-damp" by the miners, while the carbon dioxide, which is formed when it burns and is left in the mine after an explosion, is called "choke-damp." The critical temperature of methane is  $-82^\circ$  and its critical pressure 56 atmospheres; its boiling-point is  $-164^\circ$ . Because of its very low critical temperature, the methane of natural gas does not exist in the depths of the earth in a liquid condition, but is present simply as a highly compressed gas, filling the pores of the rocks.

The origin of methane found in nature is as much in doubt as that of the other hydrocarbons, but the probabilities are that it was formed by the decomposition of organic matter. It may be made by the action of water upon aluminum carbide,



and it is possible that a part of the methane has been produced by this reaction. In the laboratory the gas is usually prepared by distilling a dry mixture of sodium acetate and sodium hydroxide. The equation for the reaction is as follows,



Methane burns in the air forming carbon dioxide and water. The flame has very little luminosity, unless used with a Welsbach mantle composed of the oxides of cerium and thorium. Because of the great amount of heat which is produced during the combustion, methane is very valuable for fuel and in the form of natural gas is much used for this purpose. As will be seen by the following equation,  $\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}$  one volume of methane will require two volumes of oxygen or ten volumes of air for complete combustion. The explosive

qualities of a mixture of gas and air are utilized as a source of energy in the gas engine.

When a mixture of chlorine and methane is exposed to sunlight the four combining weights of hydrogen are successively replaced by the chlorine forming the following series of compounds:

Methyl chloride.....	$\text{CH}_3\text{Cl}$
Methylene chloride.....	$\text{CH}_2\text{Cl}_2$
Chloroform.....	$\text{CHCl}_3$
Carbontetrachloride.....	$\text{CCl}_4$

The other product of each of these reactions is hydrogen chloride. These are not ionized when dissolved in water and hence are not salts. Chloroform is perhaps the most important of these substances and is generally prepared by the action of bleaching powder upon ordinary alcohol. It is a colorless, easily volatile liquid which is used as a solvent and as an anesthetic. Carbon tetrachloride is now being manufactured on a large scale, but not directly from methane. It is a valuable solvent and finds many applications as such, being used as a substitute for gasoline in dry cleaning, because it has the great advantage that it is not inflammable. In fact it is now being used as a fire extinguisher and is about the only thing beside carbon dioxide which will put out a gasoline fire.

**Radicals.**—A study of the derivatives of methane reveals the existence of a series of compounds which have the common characteristic that their formulas can be so written that each contains a  $\text{CH}_3$  group,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ ,  $\text{CH}_3\text{I}$ ,  $\text{CH}_3\text{OH}$ ,  $(\text{CH}_3)_2\text{O}$ . When these compounds undergo certain transformations the  $\text{CH}_3$  group seems to pass unaltered from compound to compound and so acts like a chemical individual, being like the ammonium ion in this respect. A group which behaves in this way is called a radical, and this particular group,  $\text{CH}_3$ , is known as the methyl radical. A study of the chemistry of the carbon compounds shows that we have to do with a large number of such radicals. For example, each member of the paraffin series will form a monovalent radical, which contains one less atomic weight of hydrogen per mole than the hydrocarbon from which it was formed. Ethane,  $\text{C}_2\text{H}_6$ , forms the ethyl radical,  $\text{C}_2\text{H}_5$ ,

propane,  $C_3H_8$ , yields the propyl radical,  $C_3H_7$ , etc. These radicals, which we have been considering are not ions, and have the remarkable property of being able to combine with almost any element or radical irrespective of the electrical character of the substance. For example, the ethyl radical will combine with sodium to form sodium ethyl,  $C_2H_5Na$ , or with chlorine forming ethyl chloride,  $C_2H_5Cl$ , and yet sodium may be considered a typical electropositive element, while chlorine seems to be decidedly electronegative, at least in the chlorides. This tendency toward universal combination exhibited by these radicals is apparently one of the causes for the great variety of carbon compounds. The methyl radical, for example, will combine with chlorine, bromine, or iodine, forming methyl chloride, bromide, or iodide, with the hydroxyl, producing methyl alcohol,  $CH_3OH$ , and with oxygen yielding methyl ether  $(CH_3)_2O$ . If no other substance is present for it to combine with, one methyl radical will combine with another to form the compound  $CH_3 - CH_3$  or  $C_2H_6$ , which is ethane, and this in turn will yield the ethyl radical,  $C_2H_5$ , which under the proper conditions will combine with a methyl radical to form the compound,  $C_2H_5CH_3$ , or  $C_3H_8$ , which is propane, the third member of the group. Proceeding in this way, practically the whole series of paraffin hydrocarbons has been built up and consequently they all may be regarded as derivatives of methane.

**Other Hydrocarbons.**—Among the hundreds of hydrocarbons, mention may be made of benzene,  $C_6H_6$ , and toluene,  $C_6H_5CH_3$ . These are obtained by the distillation of coal and are of great importance because they are the starting-points for the preparation of a great many very useful substances. From benzene we may make carbolic acid,  $C_6H_5OH$ , aniline,  $C_6H_5NH_2$ , and the aniline dyes. Toluene yields among other compounds, trinitrotoluene,  $C_6H_2(NO_2)_3CH_3$ , which is a powerful explosive.

**Types of Carbon Compounds.**—The principal carbon compounds with which we shall have to deal may be divided into a few well-marked types; the hydrocarbons, which we have already discussed, alcohols, ethers, aldehydes, acids, esters and carbohydrates. The following table gives the general formulas for these compounds. In this table "R" stands for any monovalent radical, and "A" for the anion of a monobasic acid.

Type	General formulas
hydrocarbons.....	RH
alcohols.....	ROH
ethers.....	R <sub>2</sub> O
aldehydes.....	RCOH
acids.....	RCOOH
esters.....	RA
carbohydrates.....	C <sub>m</sub> H <sub>2m</sub> O <sub>n</sub>

**The Alcohols.**—The first member of the alcohol group, methyl or wood alcohol, CH<sub>3</sub>OH, is one of the by-products obtained in the destructive distillation of wood for charcoal. It is a colorless liquid, which boils at 66°. It is valuable as a fuel and as a solvent. It is decidedly poisonous and is largely used in the crude state to mix with ethyl alcohol for the production of the so-called denatured alcohol.

The molecular weight and analysis of methyl alcohol show that it contains per molecule one atom each of carbon and oxygen and four of hydrogen. Experience teaches that one of the hydrogens is different from the others, because sodium will replace only one, forming the methyllate, CH<sub>3</sub>ONa, and further that hydrochloric acid will react with the alcohol, yielding water and methyl chloride, CH<sub>3</sub>Cl. To represent the action with sodium, one of the hydrogens must be written differently from the others, say HCH<sub>3</sub>O; but the action with the acid suggests a

hydroxide, and the formula, CH<sub>3</sub>OH or  $\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\text{OH} \\ | \\ \text{H} \end{array}$ , indicates

both actions, and the latter is called the structural formula for methyl alcohol. In a similar way, the properties of other compounds are studied, and structural formulas devised to represent them.

**Ethyl alcohol**, C<sub>2</sub>H<sub>5</sub>OH, or grain alcohol as it is called, is formed by the action of an enzyme or catalyzer produced by yeast upon sugars, C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>. The process is called fermentation and the equation for the reaction is as follows:



The alcohol so formed may be largely separated from the water by distillation, the alcohol passing over first since its boiling-point is  $78.3^{\circ}$ . The alcohol of commerce contains about 95 per cent by volume of alcohol and 5 per cent. of water. It is not possible to separate these two substances completely by distillation, since they form a minimum boiling mixture, boiling at  $78.15^{\circ}$  and containing 4.43 per cent. of water. (See hydrogen chloride and water.) Absolute alcohol free from water may be obtained by adding unslaked lime to the 95 per cent. alcohol. The lime combines with the water to form calcium hydroxide, and after the action is complete, the absolute alcohol may be distilled off. The density of alcohol at  $25^{\circ}$  is 0.7851. Alcohol is a valuable fuel and an extremely useful solvent for many substances which are difficultly soluble in water. It is largely employed for the preparation of medicines. **Denatured alcohol** is 95 per cent. alcohol, mixed with some substance which cannot be readily separated from the alcohol and which will render it totally unfit for use as a beverage. A very commonly used formula is 89.5 per cent. grain alcohol, 10 per cent. wood alcohol and 0.5 per cent. benzine. Such alcohol is exempt from the payment of any internal revenue tax, and is consequently much cheaper than the pure article, and so finds extensive application in the arts.

**The Ethers.**—The general formula for these substances is  $R_2O$ . Ethyl ether,  $(C_2H_5)_2O$ , is the best known and by far the most important member of this group. It is prepared by heating a mixture of ethyl alcohol and sulfuric acid to  $140^{\circ}$ . The equation is



The sulfuric acid acts as a catalyzer and will change many times its own weight of alcohol into ether. Ethyl ether is a colorless liquid boiling at  $34.6^{\circ}$ . It is used as solvent for fats, etc., and as an anesthetic.

**The Aldehydes.**—The general formula for the aldehydes is  $RCOH$ . These substances, in general, may be formed by the partial oxidation of the alcohols. The first member of the series is formaldehyde,  $HCOH$ . In this case hydrogen takes the place of the "R" in the general formula. Formaldehyde is produced by the incomplete combustion of methyl alcohol when the vapors

this substance mixed with air come in contact with platinum gauze or platinized asbestos. Formaldehyde is gaseous at ordinary temperatures, the boiling-point being  $-21^{\circ}$ ; it has a very pungent, irritating odor, is quite soluble in water and is put on the market in a 40 per cent. solution, known as formalin. Both the solution and the gaseous substance are powerful germicides and are used as disinfectants.

**The Acids.**—The general formula for the organic acids is  $\text{COOH}$ . These substances are numerous and important. The first member of the series is formic acid,  $\text{HCOOH}$ . As in the case with formaldehyde, in the formic acid the hydrogen takes the place of "R" in the general formula. Sodium formate,  $\text{HCOONa}$ , is made by passing carbon monoxide over heated sodium hydroxide, the equation being

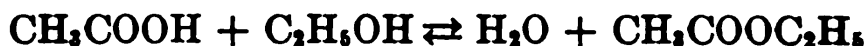


From this salt, the acid may be obtained by distilling it with dilute sulfuric acid; concentrated sulfuric acid decomposes formic acid into water and carbon monoxide. It is a colorless liquid boiling at  $100^{\circ}$ , freezing at  $8.6^{\circ}$ . Like almost all other carbon acids it is a weak acid, although somewhat stronger than acetic acid which is the next member of the series. In spite of the fact that, as its formula indicates, it contains two atomic weights of hydrogen per mole, it is a monobasic acid, only one of the hydrogens being ionizable. This fact that the hydrogens differ in their properties is expressed by writing them in different positions in the formula— $\text{HCOOH}$  instead of  $\text{COOH}_2$ . As indicated by the general formula for the series, the organic acids contain the group  $\text{COOH}$ , and to this is ascribed their acid character, and the hydrogen of this group is supposed to be that which ionizes.

**Acetic Acid.**—Acetic acid,  $\text{CH}_3\text{COOH}$ , is the second member. It is formed during the destructive distillation of wood, and is one of the valuable by-products of this process. Large quantities of the substance are produced by the oxidation of ethyl alcohol by the oxygen of the air with the aid of a certain form of bacteria, known as *B. Aceti*. The common name for this is mother of vinegar. The dilute solution of acetic acid, formed by the oxidation of the alcohol contained in cider, is known as

vinegar. Vinegar usually contains 4 to 5 per cent. acetic acid. Pure acetic acid is a colorless liquid which boils at  $119^{\circ}$  and freezes at  $16.7^{\circ}$ . It mixes with water in all proportions. As has been mentioned repeatedly acetic acid is a weak acid, being only slightly dissociated. Although it contains four atomic weights of hydrogen per mole, it is a monbasic acid, three of the four atomic weights of hydrogen being present in the methyl radical, and these are non-ionizable.

**The Esters.**—When an alcohol is acted upon by an acid, a reaction takes place which consists in the formation of water, apparently from a combination of the acidic hydrogen of the acid with the hydroxyl of the alcohol, and of an ester—a compound produced by the union of the radicals from the acid and the alcohol. The equation for the reaction between ethyl alcohol and acetic acid is as follows:



$\text{CH}_3\text{COOC}_2\text{H}_5$  is called ethyl acetate, and is an important member of the group of esters. Many of these are pleasant smelling substances and are largely responsible for the odors and flavors of our flowers and fruits. In addition the fats and vegetable oils are esters of the alcohol glycerine, so one of our most important classes of foods is composed of esters.

**Carbohydrates.**—The carbohydrates are an extensive group of carbon, hydrogen and oxygen compounds in which, with very few exceptions, the hydrogen and oxygen are present in the same relative proportions as in water, so that the general formula for nearly all members of the group may be written  $\text{C}_m\text{H}_{2m}\text{O}_m$ . The great importance of this class of compounds will be recognized at once when it is known that it includes sucrose (cane or beet sugar)  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$ , starch,  $(\text{C}_6\text{H}_{10}\text{O}_5)_x$ , and cellulose,  $(\text{C}_6\text{H}_{10}\text{O}_5)_y$ . Cotton and linen are practically pure cellulose, and the woody part of all plants consists largely of this substance. In wood it is associated with another compound called lignin of unknown composition. If the wood is treated with a solution of sodium or calcium acid sulfites the lignin is dissolved and the cellulose is left behind in fine fibers suitable for making wood pulp paper. Starch is obtained from many plants,

chiefly corn, wheat, potatoes and rice. Its importance as a food and for laundry work is well known.

When boiled with a dilute acid starch takes up water and changes to glucose; a thick syrup of the latter made from corn starch is often called corn syrup. Cane and beet sugar are identical; their source and general properties are too well known to require discussion beyond the fact that when boiled with dilute acid, water is taken up and a solution of glucose and fructose is formed. This process is called inversion of sugar and the product is known as invert sugar.

**Some Explosives.**—The importance of explosives for industrial and war-like purposes is universally recognized. Besides the old-fashioned gunpowder (p. 300), and nitroglycerine (p. 207), there may be mentioned the following: **Guncotton**,  $[C_{12}H_{14}O_4(NO_3)_6]_x$ , is made by acting on cotton with a mixture of nitric and sulfuric acids. It is very explosive and is used in making smokeless powders; one form of these is known as walsrode. It is made of a mixture of 99 per cent. guncotton, and 1 per cent. ethyl acetate. **Picric acid**,  $C_6H_2(NO_2)_3OH$ , is made by acting on phenol, i.e., carbolic acid,  $(C_6H_5OH)$ , with nitric and sulfuric acids. It is the explosive known as lyddite. **Trinitrotoluene**,  $C_6H_2(NO_2)_3CH_3$ , is made in the same way using toluene,  $C_6H_5CH_3$ , in place of phenol. It is known as T.N.T. It may be melted and poured into shells. When it explodes, great volumes of black smoke are produced. **Dynamite** is nitroglycerine absorbed in some porous material such as finely divided silica, kieselguhr as it is called. Nitric acid is used in the preparation of each of these explosives, and this is one reason for its great industrial importance.

**Unsaturated Hydrocarbons.**—The methyl radical may be imagined as being formed from methane by the dropping of one atomic weight of hydrogen from this substance. If two were removed the divalent radical  $CH_2$  would be produced. This radical is known as methylene and forms a long series of compounds similar to those of methyl, but differing of course because of the fact that the radical is divalent. The chloride, for example, is  $CH_2Cl_2$ . Under proper conditions two of these methylene radicals will combine for the formation of the substance  $C_2H_4$ , which is known as ethylene. This is the first member of a long series of hydrocarbons, known as the ethylene series.

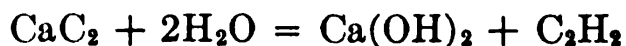
These compounds have the property of combining directly with two atomic weights of hydrogen forming members of the paraffin series. Because of the fact that they are capable of taking up more hydrogen they are called "unsaturated" hydrocarbons. They are also able to combine directly with two atomic weights of a halogen per mole of hydrocarbon. Ethylene, the first member of the series, is formed by heating ethyl alcohol with sulfuric acid to a temperature of  $175^{\circ}$ . The apparent reaction is



but it probably goes in steps, intermediate compounds involving the sulfuric acid being formed. It is a colorless gaseous substance and boils at  $-102^{\circ}$ . Ethylene is a valuable constituent of ordinary coal gas, since it burns with a strongly luminous flame, and contributes largely to the luminosity of the gas when burned with the ordinary lava tip.

**Acetylene.**—If we imagine three combining weights of hydrogen removed from methane, the trivalent radical CH would be produced. Two such radicals by their combination would form the substance  $\text{C}_2\text{H}_2$ , or acetylene. This compound is still more highly "unsaturated" than ethylene. It is the first member of another series of unsaturated hydrocarbons, known as the acetylene series. Acetylene is a colorless gas, which burns with an intensely luminous flame. When burned with oxygen in a properly constructed burner it will produce a very high temperature. Use is made of this in the metal-working trades for the autogenous welding of metals and also for the rapid cutting of steel, etc., by burning a path through it.

Acetylene is prepared by the action of water upon calcium carbide,  $\text{CaC}_2$ , the equation being as follows:



When mixed with air, in any proportions between 2.53 per cent. and 73 per cent. acetylene will explode. These limits are wider than for any other gas. A mixture of natural gas and air, for example, explodes only when it contains from 5 to 15 per cent. of methane,  $\text{CH}_4$ . Liquid or highly compressed acetylene is explosive even when unmixed with air, because it is formed from its elements with the absorption of much heat; so if decomposition

once starts, the heat evolved will raise the temperature and make the reaction go faster. This is the case with all explosives.

Acetylene is very soluble in an organic substance called acetone,  $(\text{CH}_3)_2\text{CO}$ , which belongs to a group of compounds called the ketones, which we have not discussed. This solution in acetone is not explosive and cylinders containing it under pressure are used to supply acetylene for the lights on automobiles and for the illumination of isolated residences.

**Fuel Gases.**—Gaseous fuels are of great importance for domestic and technical purposes because they are clean and very easily controlled. They are also finding a rapidly increasing use as a source of energy in gas engines, so that the subject of fuel gases is one of no little practical importance. Many different varieties of gas are in use such as natural gas, coal gas, wood gas, oil gas, and the various types of water and producer gases. Natural gas has already been discussed. Wood and oil gases are of rather limited application, so that we will devote our attention at this point chiefly to coal, water and producer gas.

**Coal Gas.**—Coal gas is made by heating bituminous coal in closed fire clay retorts, Fig. 43. It consists principally of hydrogen, methane, unsaturated hydrocarbons and carbon monoxide, and their relative volume is in the order given. In addition to

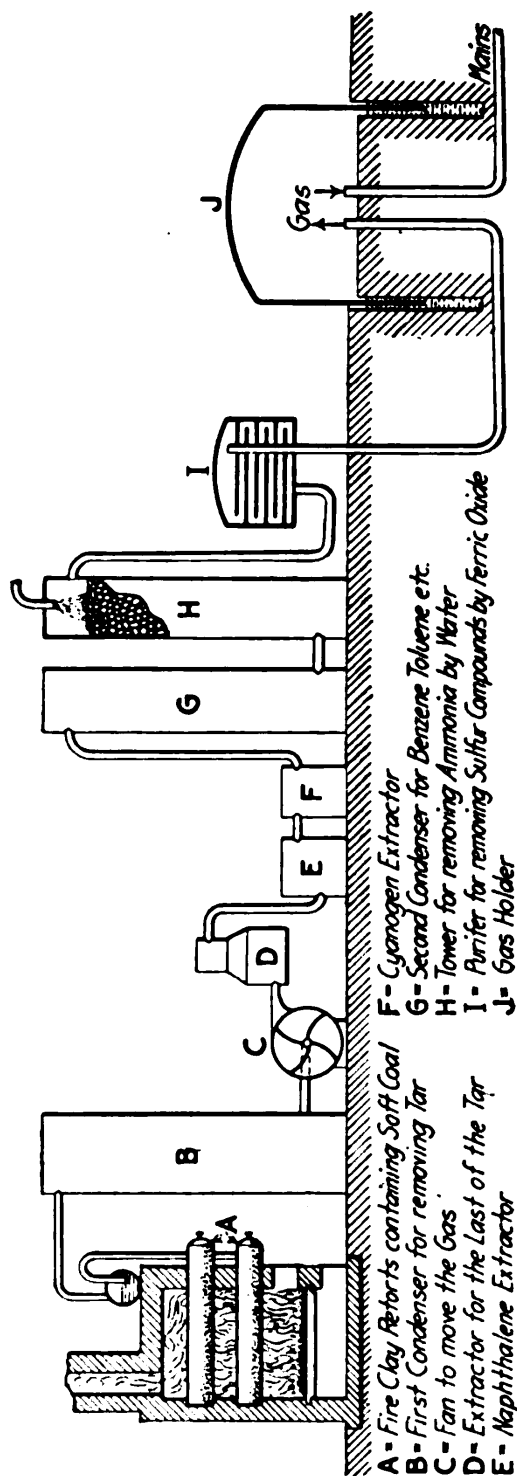
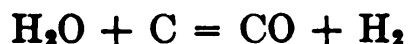


FIG. 43.

these gases, a large number of valuable by-products distil over; tar, ammonia, benzene, carbolic acid, etc., and are removed in the purification of the gas. Coke is left in the retorts.

**Water Gas.**—When steam is passed over heated coal or coke, carbon monoxide and hydrogen are formed, if the temperature is high,



or carbon dioxide and hydrogen if the temperature is lower,

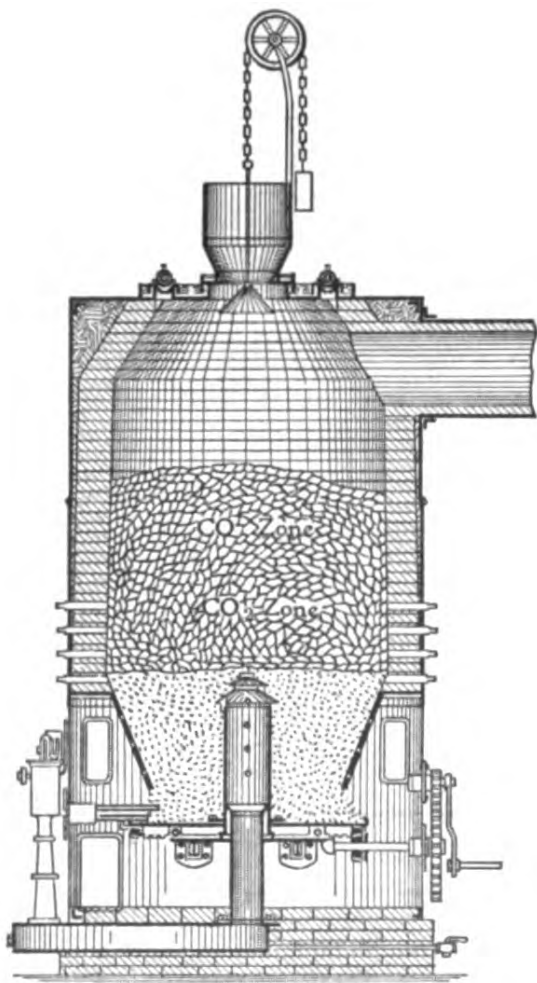
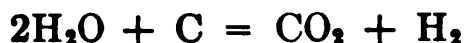


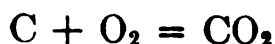
FIG. 44.

The gaseous mixture obtained in this way usually runs about 50 per cent. hydrogen and 40 per cent. carbon monoxide. It is very valuable for fuel and power purposes.

The water gas process has a great advantage over that for coal gas inasmuch as in the former nearly all of the carbon is converted into gas, while in the latter most of it remains as coke.

**Producer Gas.**—Producer gas is perhaps the most important fuel gas for industrial and power purposes. It is made by two slightly different methods. In the first, air is blown up through a deep bed of highly heated coal in a great stove-like furnace called a producer (Fig. 44). Where the air first enters, the

coal burns to carbon dioxide,



As the latter is carried up through the bed of carbon, it is reduced to carbon monoxide,



This carbon monoxide mixed with the nitrogen of the air and some unreduced carbon dioxide constitutes the producer gas as made by this method.

The second method is just the same as the first except that some steam is blown in with the air and the reactions are those just given together with the ones for water gas. The reactions for the first method evolve heat, while those for water gas absorb it. By combining the two, a greater amount of the energy of the coal is obtained in the gas than by either alone. The gas made in this way contains carbon monoxide, hydrogen, carbon dioxide, and nitrogen.

A gas engine using producer gas will often deliver one horsepower for an hour, on a pound to a pound and a half of coal used in the producer. The fuel efficiency of such a plant is much greater than that of a steam plant.

**Blau Gas.**—Blau gas is made by cracking petroleum by heating it to a high temperature then cooling and compressing the products to 100 atmospheres. This liquefies many of the gaseous substances produced. The liquid is sold in strong steel cylinders, which may be connected through reducing valves to the pipes in the building where it is to be used. The blau gas burns with a very bright and hot flame.

## FLAMES

**Flames** are produced by the rapid interaction of two or more gases whereby sufficient heat is generated to render the gases and their products luminous. In most of the cases to which the term is applied, one gas passes in a stream into a larger body of the other and the chemical action takes place at the point of contact of the two.

In the flames with which we are most familiar, the oxygen of the air is one of the active gases and the other is hydrogen, natural gas, coal gas, or some similar mixture; and since the flame is located at the opening whence the gas issues into the air, we very naturally speak of the gas as burning, but the air has just as much to do with the phenomenon as the other gas. As a matter of fact, it is a very easy matter to burn a stream of air in an atmosphere of coal or of natural gas. All that is necessary

to do to show this is to place a wide-mouthed bottle, mouth downward (Fig. 45), upon a suitable support, and pass into it a moderate stream of gas until the air is displaced, and then light the gas as it issues from the mouth of the bottle. Now pass a glass tube from which a steady stream of air is escaping up into the bottle. As it goes up through the flame at the mouth of the

bottle, the air will take fire, and continue to burn in the gas as long as the supply of the two is kept up.

All flames give off light, but they differ enough among themselves so that we may conveniently divide them into two classes; non-luminous and luminous. This classification is arbitrary, because there is every gradation between the typically non-luminous flame of hydrogen and that of acetylene which is the most brilliant of all; that of methane stands near the dividing line.

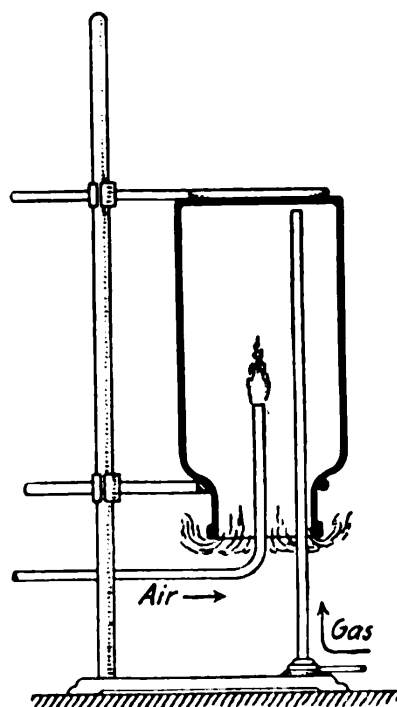


FIG. 45.

When infusible non-volatile solids are placed in non-luminous flames, they are heated to incandescence and give out light; a mixture of 99 per cent. thorium oxide, with 1 per cent. cerium oxide, is

especially brilliant under these conditions, and it is this mixture which is used in the Welsbach mantles for incandescent gas lighting.

The luminous flames are nearly all produced by the burning of compounds of hydrogen and carbon, and there is much evidence in favor of the view that solid particles of carbon are formed in their interior, and that the greater part of the light is due to the incandescence of these particles. If a cold surface be placed in such a flame, these particles will deposit on it forming a layer of soot or lampblack. In fact, this is the way in which lampblack is made.

If the flame of an ordinary hydrocarbon gas, such as coal gas issuing from a circular opening, be examined, it will be found to consist of a number of conical sheaths or zones fitting one inside the other as indicated in the diagram (Fig. 46). In the relatively

non-luminous sheath "a" water and carbon dioxide are formed, and the heat from this radiating inward decomposes the hydrocarbon toward the base of the flame forming hydrogen and acetylene, or hydrogen, methane and acetylene; as the gases pass upward the temperature rises and finally reaches a point where the acetylene rapidly decomposes into hydrogen and carbon. Since this is a reaction which takes place with the evolution of heat, the temperature of the particles of carbon is raised even above that of the rest of the flame, and this is the cause of the greater part of the light. These changes take place in the zone "b." As the carbon passes up through the flame, it gradually burns, first to the monoxide, then to the dioxide. In the interior of the flame, where the supply of oxygen is limited, the carbon is practically all burned to carbon monoxide before the hydrogen burns. The luminosity of a flame may be increased by putting both gases under greater pressure, or by heating the

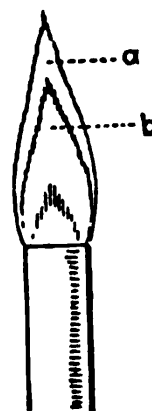


FIG. 46.

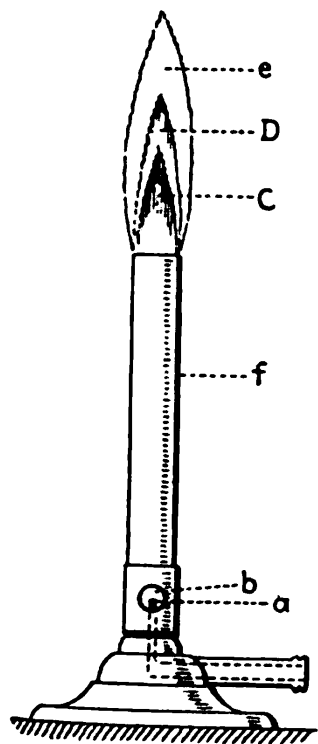


FIG. 47.

gas before it leaves the burner. On the other hand, anything which will lower the temperature of the flame will decrease the light. This may be done by holding a cold object in the flame or by mixing some indifferent gas such as nitrogen with the combustible gas. This both dilutes the gas and makes more material to be heated, and hence makes the flame colder.

**Bunsen Burner.**—Robert Bunsen, a German chemist, invented the burner which bears his name, in order to burn coal gas with the clean smokeless flame, which is so desirable for chemical purposes. A diagram of the burner and its flame is shown in Fig. 47. The gas enters the burner through the jet "a," and, having a high velocity, it draws a certain quantity of air in at the holes "b" in the base of the tube "f." In passing up through this tube, the gas and the air mix. Three well-marked sheaths are formed in the flame. "C" is non-luminous, and so cold that a

match head may be held in it for some time without igniting. In this, practically no chemical change takes place. "D" is bluish-green and very hot, especially at the upper tip, but not very luminous. In it the hydrocarbons are transformed into carbon monoxide and hydrogen. In the outer layer "e" the hydrogen and carbon monoxide burn to water and carbon dioxide. The non-luminous flame of the Bunsen burner is smaller and hotter than a luminous flame burning the gas at the same rate.

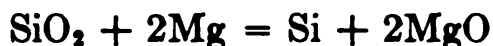
## CHAPTER XVII

### SILICON

**General.**—Silicon, the second member of the carbon group, occurs very abundantly in nature in the form of its oxide and various silicates. This element, next to oxygen, is present in the earth in the greatest quantity, forming as it does about one-fourth of the earth's crust.

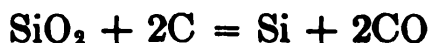
**Preparation.**—Silicon exists in at least two allotropic modifications, one crystalline, the other amorphous. Some evidence also points toward the occurrence of two distinct crystalline forms, corresponding to graphite and diamond.

Amorphous silicon may be prepared by heating finely powdered quartz, which is silicon dioxide,  $\text{SiO}_2$ , with metallic aluminum or magnesium; the reaction which takes place with magnesium is represented by the following equation,



The magnesium oxide is removed by treating the resulting mixture with hydrochloric acid.

Crystalline silicon is now being prepared on a large scale at Niagara Falls by reducing the dioxide with carbon in an electric furnace. It is used in the manufacture of steel.



An alloy of silicon and iron known as ferrosilicon is also used in making steel. It is made by heating together sand, iron oxide and carbon in an electric furnace.

**Properties.**—Amorphous silicon is a dark brown, friable substance without luster, is a non-conductor of electricity, and has a density of 1.8. If the temperature is raised somewhat it takes fire and burns. The crystalline silicon is very much more resistant chemically and is not attacked by oxygen even at red heat. It is dark steel gray in color and forms opaque octahedra possessing a metallic luster, its density is 2.35.

Both varieties melt at temperatures in the neighborhood of 1,500° to a steel blue liquid which on solidifying always produces the crystalline form. Silicon dissolves in hydroxides of the alkali metals with the evolution of hydrogen and the formation of the corresponding alkali silicates.



This reaction is used to make hydrogen for filling balloons and air ships. Silicon is not soluble in any single acid but is in a mixture of nitric and hydrofluoric acids, forming silicon tetrafluoride, and is slowly oxidized by aqua regia to silicic acid.

**Silicon Dioxide.**—Silicon forms with oxygen one well-defined compound, silicon dioxide,  $\text{SiO}_2$ , which is analogous to carbon dioxide. The monoxide, the analogue of carbon monoxide, has been stated to exist and has been described as a brown powder, but as yet this has not been sufficiently confirmed. Silicon dioxide or silica, as it is commonly called, occurs very abundantly on the earth's surface both in the crystalline and the amorphous modifications. The purest form is rock crystal, which is colorless quartz. This compound when colored by different metallic oxides gives rise to smoky quartz and other semi-precious stones. Flint occurs widely distributed in nature, and is rather impure amorphous silica; other forms of this variety are certain kinds of petrified wood, opal and jasper.

On account of its extreme hardness and its transparency, rock crystal finds extensive use in the manufacture of fine lenses. Many laboratory utensils are now made from quartz. When heated before the oxy-hydrogen blowpipe it behaves like glass, in that it becomes pasty and does not pass directly from the solid to the liquid state. In this condition it may be worked and blown into the desired shapes. These vessels are very resistant chemically to nearly all reagents except the alkalies, and consequently they may replace the more expensive platinum in many operations. The temperature coefficient of this fused silica ware is very small, and a crucible heated to redness may be plunged into cold water without being broken.

**Silicic Acid and Silicates.**—Silicates are known which correspond to an even greater variety of silicic acids than there are

phosphoric acids. We have for example, salts of orthosilicic acid,  $\text{SiO}_4$ ; meta silicic acid,  $\text{H}_2\text{SiO}_3$ ; diortho silicic acid,  $\text{H}_6\text{Si}_2\text{O}_7$ ; meta silicic acid,  $\text{H}_2\text{Si}_2\text{O}_5$ ; and trisilicic acid,  $\text{H}_4\text{Si}_3\text{O}_8$ . When a soluble silicate is treated with an acid, the solution usually remains clear for a time; and then there is precipitated a difficultly soluble silicic acid whose composition is rather variable but which tends to approach that of meta silicic acid,  $\text{H}_2\text{SiO}_3$ . When heated, this yields the dioxide and water.

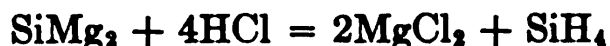
By proper manipulation, a colloidal solution of silicic acid may be prepared. A colloidal solution is one which appears perfectly homogeneous to the eye, and which will pass through a filter, but which has the same boiling- or freezing-point as pure water. When a beam of very strong light is sent through the solution and a microscope focused upon its path, a multitude of particles are seen, so extremely minute that they cannot be perceived in any other way. A true solution is homogeneous even when examined in this way. This shows that the solute in a colloidal solution is not really in solution, but that it is merely very finely divided and in a state of suspension.

A few of the naturally occurring silicates will be mentioned at this point merely to show how important to us these compounds are. Clay, mica, asbestos, serpentine, and feldspar, are among the principal silicates; while granite (a mixture of quartz, feldspar, and mica), basalt, porphyry, lava, pumice stone are also common silicate rocks. Sandstone consists principally of particles of silicon dioxide cemented together with calcium carbonate, iron oxide, or amorphous silica from silicic acid.

When exposed to the weather, the silicate rocks are gradually disintegrated under the combined action of water, carbon dioxide, changes of temperature, freezing and thawing, with the formation of clay (aluminum silicate), silica, and the carbonates of the metallic elements of the silicates. Under proper conditions, these products of disintegration will solidify into what are known as the sedimentary or secondary rocks, while the original silicates are called the igneous or primary rocks.

**Silicon Hydride.**—If in the preparation of silicon by means of metallic magnesium an excess of the metal is used, a compound magnesium silicide,  $\text{SiMg}_2$ , is formed. This compound reacts with hydrochloric acid yielding magnesium chloride and a gas

which on contact with the air takes fire spontaneously forming smoke rings of silicon dioxide.



This gas is silicon hydride,  $\text{SiH}_4$ , the analogue of methane, and like phosphine, if carefully purified, loses the property of spontaneous inflammability, which property is probably, in this case also, due to the presence of some higher hydride.

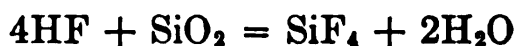
**Halogen Compounds.**—If amorphous silicon be treated with chlorine, or if a current of chlorine be passed over a mixture of finely powdered quartz and carbon which is strongly heated, the compound silicon tetrachloride,  $\text{SiCl}_4$ , is formed. Although in this latter reaction neither the carbon nor the chlorine alone is able to effect the decomposition of the silicon dioxide, their combined action can bring it about.



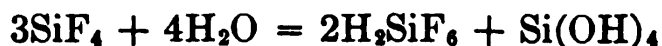
Silicon chloride is a colorless liquid whose boiling-point is  $59^\circ$ . It fumes strongly in the air since water readily decomposes it into silicic acid and hydrogen chloride.

If instead of chlorine, hydrogen chloride is passed over amorphous silicon, a compound of the composition  $\text{SiHCl}_3$  is formed and by analogy is called silico-chloroform.

Silicon unites with the other halogens to form similar compounds. The most important of these is the fluoride which is a gas at ordinary temperatures and is readily formed by treating silica or a silicate with hydrofluoric acid,



Silicon fluoride is decomposed by water, hence some dehydrating agent such as sulfuric acid must be added to remove that formed in the reaction. Silicon fluoride is most conveniently prepared by mixing together silicon dioxide and calcium fluoride, and adding concentrated sulfuric acid to the mixture. The reaction with water is unlike that of the other halogen compounds. Instead of silicic acid and hydrogen fluoride, we have the complex hydrofluosilicic acid formed according to the equation,



the lead salt of this acid is used in the electrolytic purification of lead (see p. 417).

**Carborundum.**—Carborundum is the trade name for silicon carbide,  $\text{SiC}$ . It is chemically resistant, so hard it will scratch glass, and is used very largely as an abrasive. It is not attacked by acids but is gradually decomposed by fused alkalis forming the respective carbonate and silicate.

Carborundum is prepared on a large scale at Niagara Falls by heating together in an electric furnace (Fig. 48), carbon, sand and sawdust with common salt as a flux. The electric current is passed through the carbon core, T (Fig. 48), until the mix-

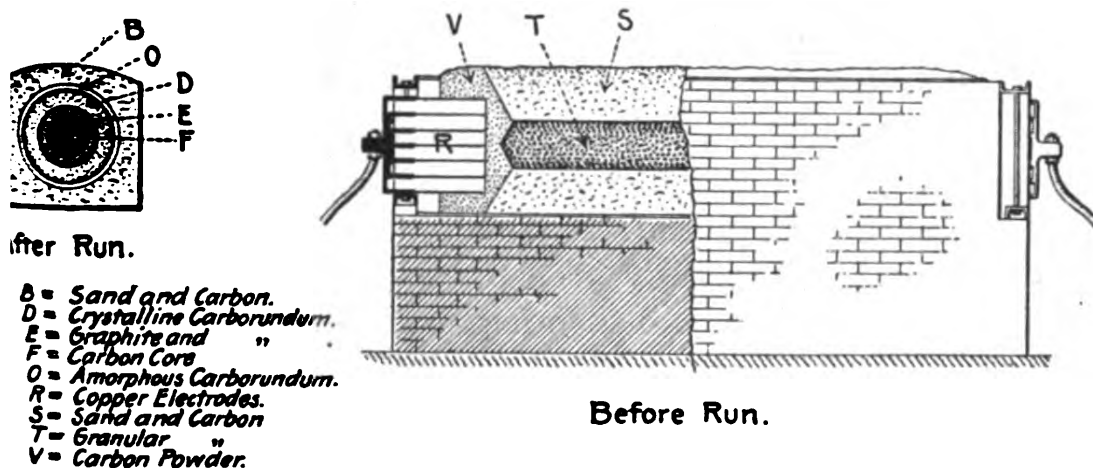


FIG. 48.

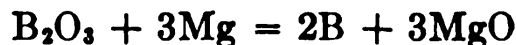
ture of carbon, sand, etc., has been heated sufficiently. The furnace is then allowed to cool when a cylinder of crystallized carborundum will be found surrounding the carbon core. It is then crushed, treated with sulfuric acid to remove impurities such as iron oxide, washed and graded. The product is then worked up into abrasive wheels, hones and the like. For this purpose the carborundum is mixed with a suitable binding material such as china clay and feldspar, molded and baked at a high temperature.

## CHAPTER XVIII

### BORON

**General.**—Boron is very similar to silicon in properties, both of the free element and of its compounds. The formulas of these latter, however, together with some other considerations connect it quite closely with certain of the true metals. It occurs in nature as boric acid,  $\text{H}_3\text{BO}_3$ , the salts of this acid, and as the anhydride or boron trioxide,  $\text{B}_2\text{O}_3$ . From these it will be seen that unlike silicon, boron is trivalent. The free element may be prepared in both the crystalline and amorphous varieties as in the case of silicon, and the method is much the same as for that substance, viz., by the reduction of the oxide with a metal.

Fused boron has recently been prepared by reducing the trioxide with magnesium, and then heating the product to  $2000^\circ$ – $2500^\circ$  in an electric furnace when it melts.



The product is black, amorphous and very hard, scratches everything except diamond, but is rather brittle. When cold, it is a very poor conductor of electricity, but at  $400^\circ$  it conducts 2,000,000 times as well as at room temperature. Because of its great temperature coefficient, it is well adapted to the making of devices for the measurement of temperature and for the regulation of electrical machinery.

**Boric Acid.**—Boric acid, or boracic acid as it is commonly called, is formed by the action of water on the anhydride, boron trioxide. The acid corresponding by analogy to orthophosphoric acid, is  $\text{H}_3\text{BO}_3$ , and is called orthoboric acid. While this acid exists free, nearly all the known salts are formed from acids derived from  $\text{H}_3\text{BO}_3$  by the loss of water. In nature it occurs as somewhat yellowish scales. It is very soluble in hot water but much less so in cold. The aqueous solution reacts faintly acid.

On being heated, the acid passes first into water and the trioxide, which at a higher temperature melts to a glass-like mass

which is capable of dissolving metallic oxides. Upon this property depends the use of boric acid as a flux in hard soldering.

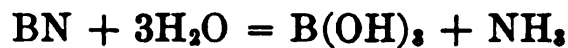
While the anhydride is fairly resistant to heat, the acid itself is volatile with steam. One of the methods for obtaining the acid depends upon this fact. In the volcanic districts, vapors containing boric acid escape from the earth. These are passed into water, condensed, and the boric acid finally becomes concentrated enough to crystallize out at lower temperatures. When boric acid is introduced into a flame it volatilizes and imparts a green color to the flame.

Of the many boric acids, we shall mention only the metaboric, formed from  $\text{H}_3\text{BO}_3$  by the loss of one mole of water, according to the equation,  $\text{H}_3\text{BO}_3 = \text{HBO}_2 + \text{H}_2\text{O}$ ; and the tetraboric formed according to the equation  $4\text{H}_3\text{BO}_3 = \text{H}_2\text{B}_4\text{O}_7 + 5\text{H}_2\text{O}$ . In any water solution of boric acid, the ions of these different acids exist in equilibrium.

The sodium salt of tetraboric acid,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  or borax, occurs in California and in others of the western states and is also manufactured by decomposing the naturally occurring calcium borate,  $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$ , with sodium carbonate and bicarbonate and recrystallizing. Borax contains either 5 or 10 moles of water of crystallization depending upon the temperature at which it is crystallized. It effloresces in the air and, if heated, swells up, then melts to a glassy substance which dissolves metallic oxides similarly to boric oxide. Some of these solutions have distinctive colors, and are used in blowpipe analysis and in making enamels. Because of the weakness of boric acid a solution of borax is hydrolized enough to be alkaline. On this account it is used to a slight extent in households to soften water, but this is a very costly method. Borax and boric acid have fairly strong antiseptic properties and are used in medicine and as preservatives.

**Other Compounds.**—The chlorides and other halogen compounds of boron may be prepared in the same way as the corresponding compounds of silicon and are similar in their properties. Since boron is trivalent their general formula is  $\text{BA}_3$ , where A represents the halogen anion. The fluoride when dissolved in water forms the compound,  $\text{HBF}_4$ , which is very much like hydrofluosilicic acid in its properties.

Boron readily combines with nitrogen to form boron nitride, BN, so unless special precaution is taken to exclude the air during the preparation of the free element, the latter is likely to be contaminated with the nitride. This compound is a white powder which when heated with water reacts to form ammonia and boric acid,



## CHAPTER XIX

### THE ARGON GROUP

The gaseous substances helium, neon, argon, krypton, xenon and niton form an interesting group of non-metallic elements which is chiefly remarkable for the fact that no compound of a member of this group has ever been prepared. Another interesting point in connection with these substances is that the element helium is certainly one of the products of the spontaneous transmutations which the radioactive element radium undergoes.

The molecular weights of these elements may be easily obtained from their gaseous densities but since they will not enter into combination with any substances, the question as to the number of atoms per molecule and hence their atomic weight is not easily answered. But in spite of their inactivity we can arrive at a reasonable conclusion through the following line of argument.

The quantity of heat necessary to raise the temperature of a gram mole of a substance  $1^{\circ}$  is called its molecular heat. If the volume is kept constant during the heating, it is known as the molecular heat at constant volume. Now it is an easy matter to determine both the molecular and atomic weights of mercury, and these turn out to be 200 in each case. In addition, the molecular heat at constant volume of mercury vapor is 13 joules. The molecular heat at constant volume of gases having two atoms per molecule such as oxygen, nitrogen, hydrogen, carbon monoxide, etc., lies between 20 and 21 joules, while that for substances having three atoms per molecule is 28 to 33 joules. The molecular heat at constant volume for the members of the argon group is 12 to 13 joules. We may therefore safely conclude that there is one atom per molecule of these elements just as is the case with mercury, and hence that their atomic and molecular weights are identical.

**Helium.**—The element helium has an atomic and molecular weight of 4.00. It is found in very small quantities in the air. It is also found in the gases of many mineral springs and is present in relatively large quantities in natural gas. The gas at Dexter, Kansas, contains as high as 1.84 per cent. of helium. Outside of natural gas, the principal source of helium is the rare minerals containing the radioactive elements radium, uranium, thorium, etc., from which it may be obtained by simply heating the mineral in a vacuum or by dissolving it in dilute sulphuric acid or fused potassium acid sulfate. The helium is simply enclosed in the mineral and is not in combination. From the fact that it occurs in those minerals which contain radium, etc., it is probable that it is formed in the mineral by the transformation of the radioactive elements. The same source is indicated for the helium of natural gas by the fact that it contains niton (see p. 265).

Helium was the last gas to be liquefied. This was done in July, 1908, by Kammerlingh Onnes. It is a clear, colorless liquid boiling at  $-268.5^{\circ}\text{C}$ . or  $4.5^{\circ}$  above absolute zero. Since its critical temperature is  $-268.0^{\circ}\text{C}$ . or  $+5^{\circ}\text{A}$ . it is a very difficult substance to liquefy. When the pressure under which it boiled was reduced to 1 cm. its boiling-point was lowered to  $3^{\circ}$  above absolute zero. This is probably about the lowest temperature which we will be able to reach unless some more easily volatile liquid than helium is discovered.

Helium under diminished pressure, glows brilliantly upon the passage of an electric discharge. Upon examining the light with a spectroscope the spectrum is found to consist of a number of bright lines, one in the yellow being especially strong (see Frontispiece). Many years before helium was discovered on the earth this line was observed in the spectrum of the sun and ascribed to a then unknown element which was called helium from the Greek name for the sun "helios."

**Neon.**—Neon has an atomic and molecular weight of 20.2. It is found in the air in slightly larger quantities than helium. It occurs along with helium in the gases of certain mineral springs and in natural gas. Its boiling-point is  $-246^{\circ}$ . It is easily liquefied in a bulb surrounded by liquid hydrogen which boils at  $-253^{\circ}$ , and is separated from helium in this way. Neither

helium nor neon is absorbed by cocoanut charcoal to any great extent, and a mixture of the two gases may be easily obtained from natural gas by absorbing the other gases in cocoanut charcoal cooled with liquid air. Recent experiments indicate that neon may be a mixture of two gases one having an atomic weight of 20 and the other of 22.

**Argon.**—The atomic and molecular weights of argon, are 39.9. It occurs in nature in rather large quantities being present in the air to the extent of about 1.3 per cent. by weight or 0.937 per cent. by volume. It boils at  $-186^{\circ}$  and freezes at  $-189^{\circ}$ . Argon was the first member of this group to be discovered, being found in 1894 in atmospheric nitrogen by Lord Rayleigh and Professor Ramsay who were seeking an explanation for the fact that atmospheric nitrogen was more dense than that from chemical sources. It is separated from nitrogen by combining the latter with metallic lithium, calcium, or magnesium at a high temperature, nitrides being formed. It is now being used in the place of nitrogen in some of the gas-filled tungsten lamps. Its spectrum is shown in the Frontispiece.

**Krypton and Xenon.**—These gases occur in the air in very small amounts. They are obtained mixed with argon, helium, and neon by the removal of the nitrogen, etc., as indicated above. They are separated in the pure state by the fractional distillation of the crude argon. Krypton has an atomic and molecular weight of 82.92 and boils at  $-152^{\circ}$ . Xenon has a molecular and atomic weight of 130.2, boils at  $-109^{\circ}$ .

**Niton or Radium Emanation.**—Radium undergoes a slow spontaneous transmutation and very gradually gives off an inert gas of the argon group which is called niton or radium emanation. Although this is chemically inactive, it is highly radioactive, (see p. 495) and changes into helium and other products at such a rate that one-half of it disappears every 3.8 days. Since it is formed so slowly from radium and decomposes so quickly, there is never very much of it available for experimentation at any one time, and Sir William Ramsay who has studied it most fully has displayed great skill in its investigation. It has been shown in spite of the fact that it is formed from one element and changes into another, that it is fully entitled to be considered a distinct element. It has its own characteristic spectrum and set of other

properties. Its molecular and atomic weights have been determined by Ramsay by weighing less than 0.0001 c.c. of the gas on a balance sensitive to less than  $\frac{1}{250,000}$  mgrm. These weights are doubtless identical and are 222.4. It boils at  $-62^{\circ}$  and freezes at  $-71^{\circ}$ . Niton is so highly radioactive that

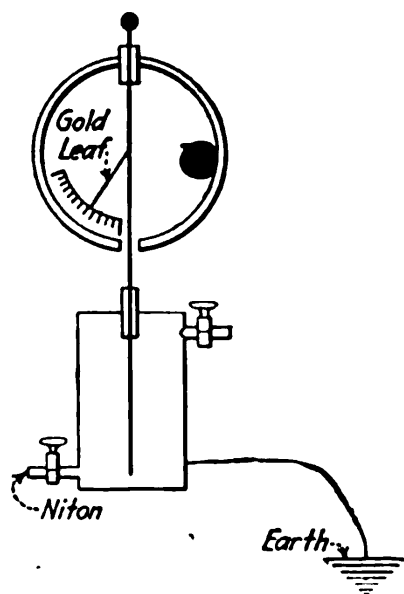


FIG. 49.

it shines in the dark, and gives out, in comparison with its mass, enormous quantities of heat. When brought in contact with chemical compounds, it very frequently decomposes them, but will not itself combine with anything. Niton is present in extremely minute quantities in air, soil, rocks, ground water, and the gases that issue from the earth. The quantity present in rocks is proportional to their radium content and furnishes the easiest method of determining the amount of radium in a rock. The rock is dissolved, the niton boiled off and passed into a charged

gold leaf electroscope (Fig. 49); the quantity of niton and therefore of radium is estimated from the rate at which the gold leaf of the electroscope collapses.

The following table giving the per cent. by volume of the inert gases in the air is based upon an estimate by Sir William Ramsay.

PER CENT. BY VOLUME OF INERT GASES IN THE AIR

Helium.....	0.00040%
Neon.....	0.00123
Argon.....	0.9370
Krypton.....	0.0094
Xenon.....	0.0011
Niton.....	Trace.

## CHAPTER XX

### THE METALLIC ELEMENTS

**General.**—In the classification of the elements it has been customary for a long time to divide them into the metals and the non-metals. We have been considering the latter in the earlier part of this book, and it now remains to discuss the chemistry of the metals. The division of the elements into these two groups is very convenient, but is entirely arbitrary as is shown by the fact that certain elements have properties in common with each group and cannot be definitively located in either.

**Characteristic Physical Properties of Metals.**—All metals when not powdered reflect so much of the light which falls upon them that they have an appearance called a metallic luster. Most are silvery white, but a few, such as gold and copper, absorb enough light to show distinct colors. But everything with a metallic luster is not a metal. The non-metal tellurium shows it, as do many compounds, especially the sulfides.

All metals are much better conductors of electricity than electrolytes are, and, unlike the latter, are not decomposed by the passage of the current, hence they are called conductors of the first class. But several of the non-metals, carbon, boron, selenium, tellurium and many sulfides are also conductors of the first class.

The metals are better **conductors** of **heat** than the non-metals, but in this respect there is not as much difference between the two groups as in the case of the conduction of electricity.

Most, but not all of the metals, are **malleable** and may be rolled or beaten into thin plates. Gold excels all the others in this respect, and may be beaten into leaves not more than 0.0001 m.m. in thickness.

Most metals are very **tenacious** and will resist a considerable force tending to pull a given piece apart. This property if

associated with the malleability mentioned above renders a metal ductile, so that it may be drawn into wire. Steel is the most tenacious of the metals, and gold the most ductile.

When metals dissolve in most solvents they lose all of their metallic characteristics, and in general form salts, but they may dissolve in one another when fused together and retain the characteristic properties of metals. The solutions of metals in one another are called alloys. As the term alloy is now used, one or more of the constituents may be a non-metal, but the whole must present the general metallic properties. Alloys which contain mercury are called amalgams. Some of these are very important.

**Characteristic Chemical Properties of Metals.**—The most noticeable chemical property of the metals is that they form simple cations, but this property is not confined exclusively to them; because the non-metals, hydrogen and tellurium also form these ions. Closely connected with the tendency of the metals to form cations is the fact that their hydroxides are generally bases while those of the non-metals are almost invariably acids; but some of the hydroxides of the metals are very weak bases, and a few act both as bases and acids. From the above facts, it may be seen that there is no sharp distinction to be drawn between metals and non-metals, so the division is purely arbitrary; but is nevertheless convenient and practicable because in the great majority of cases no hesitation is felt in making the classification.

**Distinction between Metals and Non-metals.**—If an element, when in the solid or liquid state, does not have a metallic luster and is not a conductor of electricity, it certainly is a non-metal. If it has the luster and conductivity, it may be either a metal or a non-metal and we must turn to its chemical properties for help in its classification. If it forms simple cations, it is a metal; but if it gives no simple cations and is nearly always found in anions, it is a non-metal. After all aids to classification have been applied, a few elements on the dividing will still be in dispute as to whether they are metals or non-metals, but the great majority will be definitely located.

**Classification of the Metals.**—A study of the properties of the metals soon shows that they may be divided into groups of more or less closely related elements much as was done with certain of

the non-metals. The relationship between these elements is rather tangled, however, and some of them have properties which would cause them to be placed in each of several groups and any arrangement which we make of them is more or less arbitrary. There is, however, a natural system for the classification of the elements which is called the periodic system and which includes both the metals and the non-metals. This system is based upon the observation that if the elements be arranged in the order of their atomic weights, similar elements recur at regular intervals; and if the series be broken up into periods such that each period begins with a member of a definite family, the second position in each period will be filled by a member of a closely related group of elements. The same is true for the third and following positions in the series. This may be illustrated as follows; arrange the elements in the order of their atomic weights and we have,

Position,	1,	2,	3,	4,	5,	6,	7,	8
Period No. 1.	He.	Li.	Be.	B.	C.	N.	O.	F.
Period No. 2.	Ne.	Na.	Mg.	Al.	Si.	P.	S.	Cl.
Period No. 3.	A.	K.	Ca.	Sc.	Ti.	V.	Cr.	Mn.

Choosing the members of the helium family as the elements which shall begin our periods, we find that the elements listed here fall into three periods of eight members each, and that the corresponding positions in each period are occupied by analogous elements. We can appreciate this especially for the last four members of the first two periods, since we are familiar enough with the properties of carbon and silicon to see their close relationship and similarly for nitrogen and phosphorus, oxygen and sulfur, fluorine and chlorine. That this same sort of relationship is continued over into the other periods and holds for the remaining positions in these periods, will be evident as we become more familiar with the properties of the elements. For example, lithium, sodium, potassium, etc., which occupy the second positions in the periods, form a part of a group of similar and very closely related metals as we shall soon see. In fact the relationship is fully as close as that between the halogens.

If the elements arranged in series in the order of their atomic weights be broken up into periods in the way given above and these periods be placed vertically under one another, we ob-

tain a table of the periodic classification or system of the elements. Such a table is given below. It is somewhat of a modification of one prepared by the Russian chemist, Mendelejeff in 1869, and very similar to a table published in 1870 by Lothar Meyer, a German chemist, who developed the idea independently of Mendelejeff.

An inspection of this table will show that chemically similar elements are found in vertical columns except in the case of the very last group in which the similar elements are found side by side.

In preparing this table, the principle of arrangement in the order of atomic weights has been violated in two cases. Argon with an atomic weight of 39.9 has been placed before potassium with an atomic weight of 39.1 and tellurium is put before iodine although it has the larger atomic weight. The reason for the first change is that potassium does not belong in the group of inert gases, but in with the other alkali metals in which group the argon would be entirely out of place while it goes very well with the other gases of the helium group. Tellurium and iodine are interchanged because the tellurium evidently belongs to the sulfur group and iodine to the halogen. Many researches have been undertaken to see if there was not some error in the determination of the atomic weight of either tellurium or iodine but they have led to the conclusion that tellurium actually has a higher atomic weight than iodine.

Another defect in the table is that there is no good place for hydrogen. Some have placed it at the head of the halogen family and others as the first member of the sodium group. But neither these nor any other suggestions which have been made seem to fit the case and the question of the proper location of hydrogen in the periodic system remains an open one.

There are other imperfections in the table which will become evident as we go along, but on the whole it furnishes a natural and very useful system for the classification of the elements, and it seems not unlikely that its apparent irregularities and defects will finally be found to have a great significance and to be very important.

Although each of the first eight vertical columns in the table is made up of very similar elements, a knowledge of their properties

## PERIODIC SYSTEM

	Group 0	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8
Type Compound		E <sub>2</sub> O	EO	E <sub>2</sub> O <sub>3</sub>	EH <sub>4</sub> , EO <sub>2</sub>	EH <sub>3</sub> , E <sub>2</sub> O <sub>3</sub>	EH <sub>3</sub> , EO <sub>3</sub>	EH, E <sub>2</sub> O <sub>7</sub>	EO <sub>4</sub>
Valence	0	+1	+2	+3	-4, +4	-3, +5	-2, +6	-1, +7	+8
1	He, 4	Li, 7	Be, 9.1	B, 11	C, 12	N, 14	O, 16	F, 19	
2	Ne, 20.2	Na, 23	Mg, 24.3	Al, 27.1	Si, 28.3	P, 31.0	S, 32.1	Cl, 35.5	
3	A, 39.9	K, 39.1	Ca, 40.1	Sc, 44.1	Ti, 48.1	V, 51.0	Cr, 52.0	Mn, 54.9	Fe, 55.8; Ni, 58.7; Co, 59
4	.....	Cu, 63.6	Zn, 65.4	Ga, 69.9	Ge, 72.5	As, 75	Se, 79.2	Br, 79.9	
5	Kr, 82.9	Rb, 85.4	Sr, 87.6	Y, 88.7	Zr, 90.6	Cb, 93.5	Mo, 96.0	.....	Ru, 101.7; Rh, 102.9; Pd, 106.7
6	.....	Ag, 107.9	Cd, 112.4	In, 114.8	Sn, 118.7	Sb, 120.2	Te, 127.5	I, 126.9	
7	X, 130.2	Cs, 132.8	Ba, 137.4	La, 139.0	Ce, 140.3	Nd, 144.3	.....	.....	
8	.....	.....	.....	.....	.....	.....	.....	.....	
9	.....	.....	.....	Yb, 173.5	.....	Ta, 181.5	W, 184	.....	Os, 190.9; Ir, 193.1; Pt, 195.2
10	.....	Au, 197.2	Hg, 200.6	Tl, 204.0	Pb, 207.2	Bi, 208	.....	.....	
11	Nt, 222.4	.....	Ra, 226.0	.....	Th, 232.4	.....	U, 238.2	.....	

Periods

soon shows that each group is composed of two sub-groups, and that the members of each sub-group are found in the alternate rows or periods. This is brought out in the table by setting the rows or periods alternately to the right and left of the group. As a rule, the members of each sub-group are more nearly like one another than they are like the members of the other sub-group within the family. The first member of each group usually has properties in common with both of the sub-groups and forms a connecting link between them.

Group VIII is a rather exceptional group in that it is composed of three sets of elements, each set having three members whose atomic weights, specific gravities and general properties are very similar. In this group, the elements which are most alike are found side by side, although there is also a distinct tendency toward similarity in the vertical columns.

It will be noticed that these sets of three elements come at the end of the third, fifth, and ninth series or periods of the elements.

A blank space in the table indicates that no element is known whose atomic weight and properties would give it this position. It is very probable that some of these elements will be discovered in the course of time. In the meantime it is possible to make a fairly definite prediction as to the properties of an element from those of the elements surrounding it in the table. This was done with surprising accuracy by Mendelejeff for the elements of scandium, gallium, and germanium which were unknown at the time of the publication of the table.

Not only are the chemical properties of the elements regularly recurrent or periodic functions of the atomic weights, but the same is also probably true of all measurable physical properties with the exception of the specific heat which is inversely proportional to the atomic weight for all solid elements of an atomic weight higher than 35. This is very clearly shown by Fig. 50 which represents the relation between the density of the elements in the liquid or solid state and the atomic weight and also that between the absolute temperature of fusion and the atomic weight, the former being shown by the heavy lines and the latter by the dotted lines. Most other physical properties yield similar curves and indicate clearly that the properties are periodic functions of the atomic weights.

It would be very interesting to know the proportions in which the various elements are present in the earth as a whole, but this is manifestly impossible since we have no way of getting at the composition of its interior. We can, however, get the analysis of the air, the ocean, and the rocks composing the outer 10 miles of the earth's crust, the lithosphere as it is called, and the following table (p. 274) by Clarke of the United States Geological Survey gives the results of some thousands of analyses.

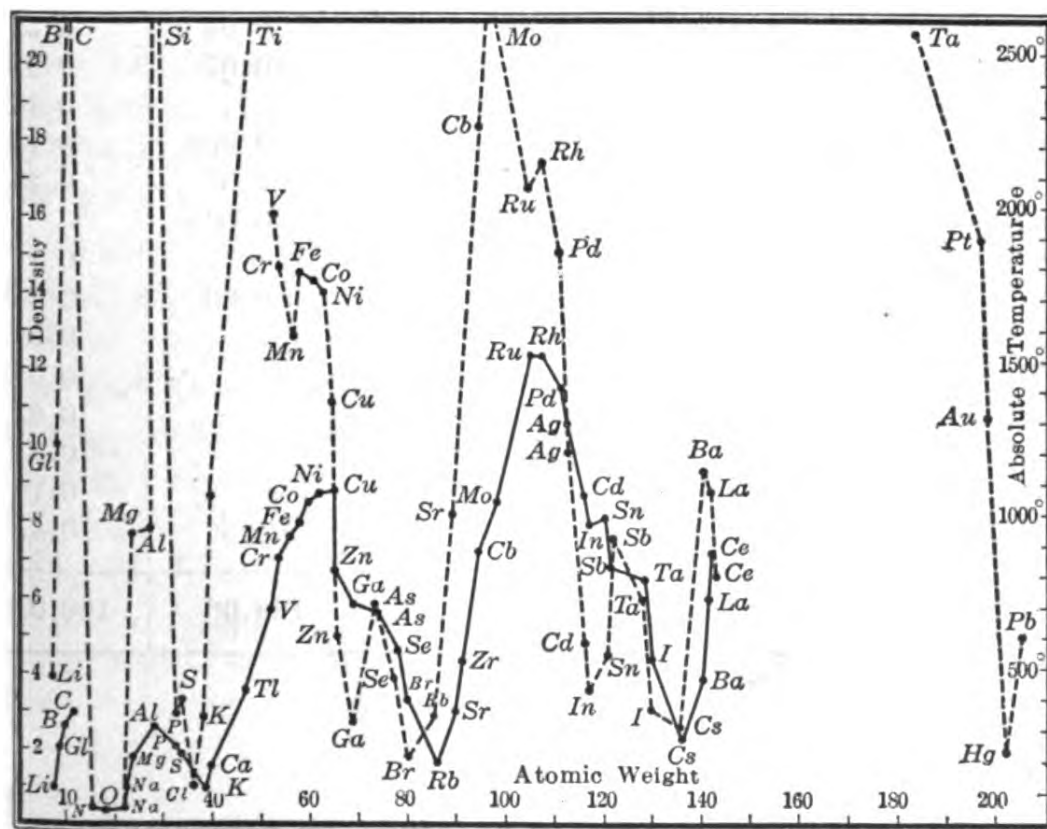


FIG. 50.

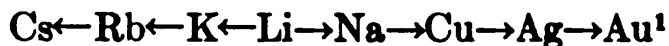
All the abundant elements have an atomic weight below 56 and the heavy metals appear to be present in very small quantities. The mean density of the earth is about twice that of the lithosphere and hence it has been supposed that the heavier elements have collected in the interior. Others ascribe the high density to the compression due to the weight of the overlying strata. This much is certain, however, that the elements cannot all be present in equal quantities by weight since their average density is greater than the mean density of the earth.

## AVERAGE COMPOSITION OF LITHOSPHERE, OCEAN, AND ATMOSPHERE

	Lithosphere (93 per cent.)	Ocean (7 per cent.)	Average in- cluding nitro- gen
Oxygen.....	47.33	85.79	50.02
Silicon.....	27.74	.....	25.80
Aluminum.....	7.85	.....	7.30
Iron.....	4.50	.....	4.18
Calcium.....	3.47	0.05	3.22
Magnesium.....	2.24	0.14	2.08
Sodium.....	2.46	1.14	2.36
Potassium.....	2.46	0.04	2.28
Hydrogen.....	0.22	10.67	0.95
Titanium.....	0.46	.....	0.43
Carbon.....	0.19	0.002	0.18
Chlorine.....	0.06	2.07	0.20
Bromine.....	.....	0.008	.....
Phosphorus.....	0.12	.....	0.11
Sulfur.....	0.12	0.09	0.11
Barium.....	0.08	.....	0.08
Manganese.....	0.08	.....	0.08
Strontium.....	0.02	.....	0.02
Nitrogen.....	.....	.....	0.03
Fluorine.....	0.10	.....	0.10
All other elements.....	0.50	.....	0.47
	100.00	100.00	100.00

## CHAPTER XXI

### THE ALKALI METALS



Group I of the periodic system is composed of the monovalent alkali metals, lithium, sodium, potassium, rubidium and cesium, and a distinct sub-group consisting of copper, silver, and gold. The alkali metals resemble one another closely, and hence may very properly be considered together. In many respects their properties are typical of the metals and a discussion of this class of elements may profitably begin with them. Copper, silver, and gold, however, differ so markedly from the alkali metals and have so many properties similar to those of metals belonging to higher groups, that it seems wise to leave their discussion to a later point.

Some of the more prominent properties of the alkali metals are given below in tabular form for sake of comparison.

Element	Atomic weight	Density	Melting-point	Boiling-point
Lithium.....	6.94	0.53	186°C.	1,400°C.
Sodium.....	23.00	0.97	97.6°	878°
Potassium.....	39.10	0.87	62.5°	758°
Rubidium.....	85.45	1.52	38.5°	696°
Cesium.....	132.81	2.40	26.5°	670°

It will be noticed that, as the atomic weight increases, the melting- and boiling-points decrease and the density increases. Sodium,

<sup>1</sup> A list of the members of each group will be given at the beginning of the discussion of the group. To save space, this will be put on one line. The member of the group having the smallest atomic weight, which is also the connecting link between the two sub-groups, will be placed about the middle of the line with the members of the two sub-families at its right or left according as they fall into the right or left hand column in the group in the periodic system.

however, is somewhat irregular in its density, a fact which may be connected with the position of sodium in the periodic system as the first member of the copper sub-group since these metals all have high densities. This individuality of sodium seems to extend to its chemical properties since potassium, rubidium, and cesium resemble one another much more closely than they do sodium.

The alkali metals are chemically the most active of this class of elements and increase in activity as their atomic weight increases. They will all decompose water, lithium rapidly and cesium with the greatest violence. In each case, hydrogen and the hydroxide of the metal is formed. These hydroxides are soluble and are strong bases, and it is this fact that gives to the sub-group the name, the alkali metals.

None of these elements is ever found free in nature, a fact which might be anticipated from their great chemical activity. Sodium and potassium are among the more common elements and do not differ much in their abundance, but owing to the fact that enormous quantities of sodium chloride have been deposited in the salt beds which are found widely distributed over the earth's surface, while only a few notable deposits of potassium salts are known, the sodium compounds are much more available and consequently much cheaper than the compounds of potassium. Since the sodium salts are fully as good as the potassium for all purposes which do not demand the presence of potassium ion, much larger quantities of the sodium compounds are manufactured and used than of potassium compounds. For this reason, the detailed discussion of the alkali metals will begin with that of sodium.

## SODIUM

**Occurrence.**—Enormous quantities of sodium compounds, chiefly the chloride, are found in sea water, and in places where some of the sea water has been cut off from the rest of the ocean and evaporated, great beds of salt have been formed. So the supply of this important substance is practically without limit.

Other important sodium compounds occur in nature in considerable quantities. These are the carbonate  $\text{Na}_2\text{CO}_3$  and the

carbonate,  $\text{NaHCO}_3$ , the nitrate,  $\text{NaNO}_3$ , cryolite,  $\text{Na}_3\text{AlF}_6$ , borax,  $\text{Na}_2\text{B}_4\text{O}_7$ , and many of the silicates.

**Preparation.**—Metallic sodium was first prepared by Davy in 1807 by the electrolysis of fused sodium hydroxide, the method which is used at the present day. Sodium hydroxide is melted in an iron vessel (Fig. 51) and electrolyzed between iron or nickel electrodes. Sodium and hydrogen are liberated at the cathode and oxygen at the anode; the metallic sodium rises to the top of the bath and collects under an iron bell-like vessel from which it is dipped from time to time. The sodium hydroxide is replaced as it is used up, thus making the process continuous. Thousands of pounds of sodium are now being made yearly by this process at Niagara Falls.

Many attempts have been made to prepare sodium by the electrolysis of fused sodium chloride, but the apparatus used has always been so short lived that the processes have not been successful.

**Properties.**—Sodium is a soft metal with a brilliant silvery white luster which is almost instantly lost upon exposure to the air owing to the formation of a film of oxide or hydroxide. It melts at  $97.6^\circ$  and boils at  $878^\circ$ . The vapor has a blue color and is exceedingly active chemically. This makes it difficult to obtain the molecular weight of sodium, but the results indicate that its value is 23, the same as the atomic weight. The metal is soluble in mercury, forming sodium amalgam. When this contains more than a small amount of sodium, it is solid. The amalgam is less active chemically than the metal itself, and finds extensive application, because, for many purposes, metallic sodium is too vigorous.

The principal chemical property of sodium is its great tendency to pass over into the ionic state. In doing this, the sodium takes up positive electricity and hence is a strong reducing agent.

Metallic sodium reacts vigorously with water, with the forma-

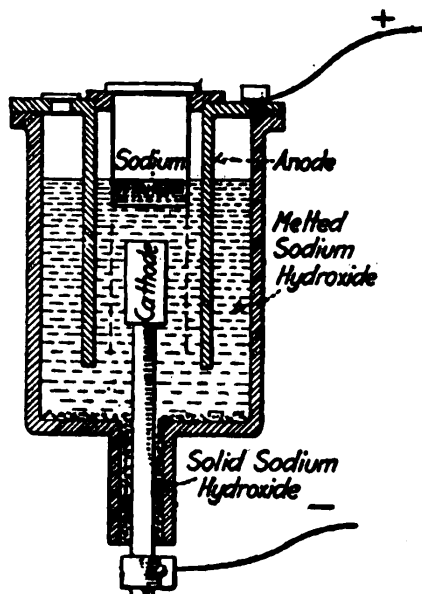


FIG. 51.

tion of sodium hydroxide and hydrogen. If more than a very small piece of sodium is used, a violent explosion is liable to occur. Ordinarily, the hydrogen evolved does not become sufficiently heated to take fire, but if the motion of the globule of sodium be diminished by placing a piece of filter paper on the surface of the water, the hydrogen catches fire and burns with a yellow flame, the color being due to the sodium.

Moist air acts rapidly upon sodium, but dry air at ordinary temperatures works very slowly. Large quantities of the metal are preserved in soldered tin cans or closely stoppered bottles. Small quantities of the metal are best kept under a petroleum oil which is without action on the metal.

When heated in the air sodium burns with a yellow flame forming the oxide and peroxide. The larger part of the sodium manufactured is used in the preparation of the peroxide and of the cyanide.

**Sodium Hydride.**—When sodium is heated to  $340^{\circ}$  in an atmosphere of hydrogen a crystalline compound,  $\text{NaH}$ , is formed. This dissolves in water with the formation of sodium hydroxide and twice as much hydrogen as an equivalent quantity of the metal. Because of the great amount of hydrogen liberated per unit weight of the substance, it has been proposed to use it as a source of hydrogen for filling balloons. In marked distinction from most of the hydrogen compounds of the non-metals, sodium hydride has no acid properties.

**Sodium Chloride.**—Sodium chloride or common salt,  $\text{NaCl}$ , may be prepared by the interaction of moist chlorine and metallic sodium or by neutralizing sodium hydroxide with hydrochloric acid and evaporating.<sup>1</sup>

However, sodium chloride is never manufactured as indicated above, because of the fact that it occurs in nature in large quantities in easily worked beds of salt. From these the salt may be taken by ordinary mining operations when it is known as rock salt; or it may be obtained by boring down into the salt bed and running water down into the boring, allowing it to stand until it is saturated with salt, then forcing or pumping out the brine and evaporating it to secure the salt. Large quantities of salt

<sup>1</sup> It is remarkable that dry chlorine will not act on sodium even at the melting-point of the latter.

$\text{Na}_2\text{CO}_3$

are obtained by the evaporation of brine from salt springs or from the ocean. Water from the ocean is usually concentrated by exposure to the heat of the sun in shallow basins constructed near the shore. The salt so obtained is called solar salt. The principal impurities contained in salt beds and brines are calcium sulfate and chloride, magnesium chloride and the bromides.

To remove these, the salt must be purified by crystallization. This cannot be done by preparing a hot saturated solution and allowing it to cool, since the salt is nearly as soluble in cold as in hot water. The salt is purified by boiling the solution which quickly causes the greater part of the calcium sulfate to precipitate, and then concentrating until most of the sodium chloride has crystallized out; but stopping the operation before the other impurities have begun to separate. Magnesium or calcium chlorides are particularly objectionable, since they cause the salt to deliquesce under ordinary atmospheric conditions. Pure sodium chloride will not deliquesce except in the very dampest weather of the summer.

The very pure sodium chloride required for many chemical purposes is obtained by dissolving the salt in water, and saturating the solution with hydrogen chloride which precipitates out the greater part of the salt. The explanation of this will be given later.

Aside from its use in food and as a preservative, sodium chloride is the source of practically all other sodium compounds and of the greater part of the chlorine and chlorine compounds of commerce. For these reasons it is a very important substance and is used by the millions of tons yearly.

**Sodium Bromide and Iodide.**—Sodium bromide and iodide are very similar to the chloride.

The solubility of the bromide is greater than that of the chloride and is in turn exceeded by that of the iodide, so it may be seen that the solubility increases as the atomic weight of the halogen increases.

Both salts are used in medicine and the bromide in photography.

**Sodium Oxides.**—Sodium monoxide,  $\text{Na}_2\text{O}$ , may be prepared by heating metallic sodium with sodium nitrate or nitrite in the absence of air. The equation for the latter reaction is as follows:

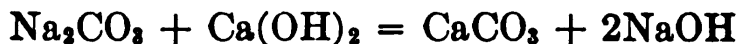


It is a gray substance which reacts violently with water to form the hydroxide NaOH.

When heated in an excess of air to 300°, sodium is oxidized to sodium peroxide, Na<sub>2</sub>O<sub>2</sub>. To carry out the process, the sodium in thin pieces is placed in aluminum trays which are slowly passed in one direction through an iron tube heated to about 300° while a current of dry air, purified from carbon dioxide, is passed in the opposite direction. This brings the air from which the oxygen has largely been removed in contact with the fresh sodium and so moderates the reaction, while the nearly oxidized substance comes in contact with the fresh air and is fully oxidized.

We have here one reacting substance moving in one direction and the other in the opposite. This arrangement is often adopted in chemical work and is known as "the principle of counter currents." The sodium peroxide so prepared finds extensive use as an oxidizing agent and as a source of oxygen, since it reacts with water with the formation of sodium hydroxide and hydrogen peroxide which then breaks down into water and oxygen. Fused sodium peroxide, known as oxone, is put on the market for this purpose. A small quantity of a copper compound is added to the peroxide to catalytically decompose the hydrogen peroxide.

**Sodium Hydroxide.**—Sodium hydroxide may be prepared by the action of the metal upon water, and is so prepared when a very pure article is required. The hydroxide obtained by this method is of course too expensive for most purposes, and the bulk of the substance must be prepared in other ways. It may be made in a purely chemical way by adding calcium hydroxide in suspension in water, milk of lime as it is called, to an 8 to 10 per cent. solution of sodium carbonate and boiling for a time. Difficultly soluble calcium carbonate is precipitated and a solution of sodium hydroxide is left:



Sodium hydroxide is also prepared by the electrolysis of a solution of sodium chloride using mercury for the cathode. Under these conditions, sodium amalgam is formed which is removed from the electrolytic chamber and allowed to react with water when hydrogen and sodium hydroxide will be formed.

The mercury freed from the sodium is returned to the electrolyzing chamber and retransformed into the amalgam. At the graphite anodes, chlorine is evolved. This process is carried out at Niagara Falls and other places where power is very cheap.

Another successful electrolytic process is that using what is known as the Townsend cell. This is shown in Fig. 52. The anode is graphite; D and D are asbestos diaphragms painted with a mixture of iron oxide, asbestos fiber, and colloidal ferric hydroxide. The cathodes are two in number, and are made of perforated plates of iron directly in contact with the diaphragms. The anode chamber is filled with brine which percolates slowly through the diaphragms and sinks to the bottom of the cathode chambers, the remaining space in these chambers being filled with kerosene. From these, the brine passes off through the goose necks, B. When the current is passed through the cell, chlorine is given off at the anode, and hydrogen and sodium hydroxide appear at the cathode. Since hydroxyl is an anion, it tends to travel toward the anode, but the brine is made to percolate through the diaphragms rapidly enough to sweep back the hydroxyl and hence prevent what would otherwise be a serious loss. The cathode solution contains both sodium hydroxide and chloride. As this is evaporated, the chloride becomes practically insoluble, and may be readily separated from the hydroxide.

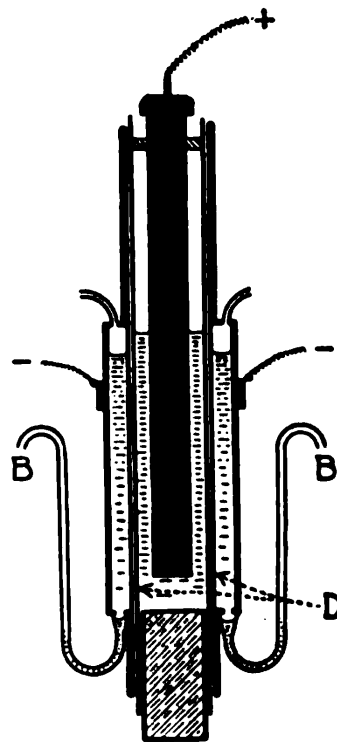


FIG. 52.

Sodium hydroxide is a deliquescent white substance which is exceedingly soluble in water. It is a very strong base and is generally used when such a substance is required as in the manufacture of soap, paper-pulp, and in many other chemical processes. It is also commonly used in the laboratory when a solution containing the hydroxyl ion is needed.

**Sodium Carbonate.**—Sodium carbonate,  $\text{Na}_2\text{CO}_3$ , has so many uses that it is almost indispensable to our civilization. It is found in nature in deposits and in solution in the lakes of the

drier parts of the earth's surface. The United States has a number of such lakes, Mono Lake and Owens Lake in California, for example. These two lakes contain over a hundred million tons of the carbonate. It can be extracted cheaply but high transportation charges prevent its general use.

The ashes of sea plants contain sodium carbonate and this was formerly the chief source of the salt. At that time this compound was at least ten times more expensive than at present and this raised the price of many other things, notably glass and soap.

The oldest practical method for the preparation of sodium carbonate from the chloride is that known as the **Le Blanc process**. It was invented by Le Blanc in 1791. The method involves essentially three steps. The first consists in the conversion of sodium chloride into sulfate,  $\text{Na}_2\text{SO}_4$ , by heating with sulfuric acid in a shallow cast iron pan a mixture of two moles of salt with one mole of "chamber" sulfuric acid. A rapid reaction takes place until half of the salt has been decomposed forming sodium acid sulfate and hydrogen chloride as shown in the following equation:



The evolution of hydrogen chloride now comes to an end and the mixture solidifies. This mixture is raked out of the pan on to

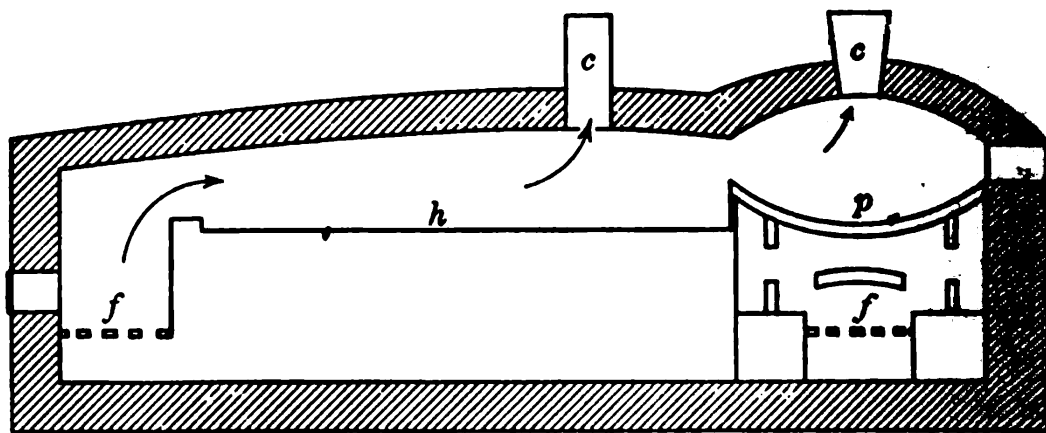


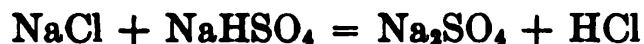
FIG. 53.

the hearth of a reverberatory furnace where it is kept well stirred by rakes and heated to a high temperature by being brought in contact with the flames and hot gases from the fire end of the furnace. Such a furnace together with the decom-

posing pan is shown diagrammatically in Fig. 53, p is the decomposing pan, h the hearth, f and f the fires and c, c the flues by which the hydrogen chloride and the products of combustion escape.

The furnace is called a reverberatory furnace because the flames are deflected by the roof and caused to play upon the hearth.

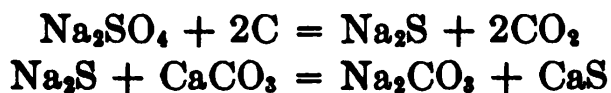
On the hearth of this furnace the sodium acid sulfate reacts with the remaining sodium chloride as shown below,



The sodium sulfate so obtained is called salt cake.

The second step consists in the reduction of the sodium sulfate to sulfide,  $\text{Na}_2\text{S}$ , by powdered coal; and the third, of the transformation of the sulfide to carbonate by heating with calcium carbonate in the form of chalk, or powdered limestone.

These two reactions are carried out at one operation by heating a proper mixture of sodium sulfate, slack coal and limestone, either in a reverberatory or in a rotary cylindrical furnace through which the flames from the fire box pass. The latter form of furnace saves the great amount of hand labor required to keep the charge stirred on the hearth of the reverberatory furnace. The equations for the reactions are,

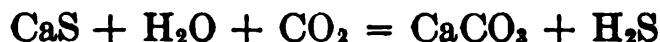


The product of this fusion is black in color and is known as black ash. It contains sodium carbonate, calcium sulfide, calcium oxide, coal, and a large number of other substances. Sodium carbonate is the only easily soluble substance present hence it is extracted from the black ash by water, using the principle of counter currents by allowing the fresh water to come in contact with the ash from which nearly all the sodium carbonate has been dissolved while the nearly saturated solution acts upon the fresh black ash. In this way, practically all the carbonate is removed from the ash and a nearly saturated solution is obtained. This solution is then evaporated and the salt separates as the monohydrate,  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ , which is called "crystal carbonate." The crystals are dried at a higher tem-

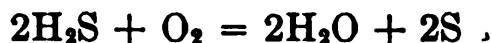
perature forming the anhydrous salt,  $\text{Na}_2\text{CO}_3$ , known as soda ash. By dissolving this in hot water and allowing it to crystallize at ordinary temperatures, the deca-hydrate,  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ , crystallizes out. This is known as sal soda, or washing soda. It dissolves more rapidly than soda ash and is largely used for domestic purposes, but contains so much water that it does not pay to ship it far.

The sulfur in the calcium sulfide must be recovered for two reasons, first, competition is very strong in the soda industry and, second, if the sulfide were exposed to the air and weather it would be gradually dissolved and pollute the neighboring streams, and since under the action of the carbon dioxide of the air and water, hydrogen sulfide would be evolved, these streams would be very offensive.

One of the best ways to recover this sulfur is to suspend the residue in water and pass in carbon dioxide from lime kilns when hydrogen sulfide is formed according to the following equation:



This hydrogen sulfide is then burned to water and sulfur in a limited supply of air,



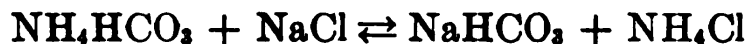
The hydrogen chloride evolved in preparing the salt cake is of course saved and either marketed as hydrochloric acid or made into bleaching powder.

The Solvay or ammonia soda process has been in successful use for more than forty years. It consists essentially in saturating a solution containing sodium chloride and ammonia in the proper proportions with carbon dioxide. When the solution becomes well saturated, solid sodium bicarbonate,  $\text{NaHCO}_3$ , begins to separate out and continues to do so until a little more than two-thirds of the sodium chloride has been transformed.

While the mechanical details of the process are so complex that some of the larger works on technical chemistry should be consulted for them, its chemistry is simple. The carbon dioxide, ammonia, and water combine to form a solution of ammonium bicarbonate,  $\text{NH}_4\text{HCO}_3$ ,



This then reacts with the sodium chloride to form sodium bicarbonate which is precipitated, and ammonium chloride which remains in solution. The equation is,



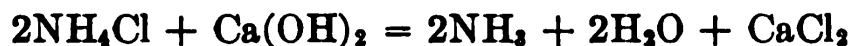
or written in the ionic form



The sodium bicarbonate is then filtered off, washed, and heated to change it into the carbonate,



The carbon dioxide so obtained furnishes a portion of that required in the process, but the greater part of the gas comes from the burning of limestone in specially designed lime kilns. The ammonium chloride which is left in the solution from which the sodium bicarbonate has separated is worth about eight times as much as the sodium carbonate which it helps to prepare, consequently the ammonia must be recovered and used again. This is done by adding slaked lime to the mother liquor and boiling off the ammonia formed, absorbing it in fresh brine and so keeping it in circulation. The equation is,



The calcium chloride so obtained is mixed with undecomposed sodium chloride and finds but little application.

The Solvay process produces much purer sodium carbonate than the Le Blanc process and is for many locations the cheaper.

**Properties of Sodium Carbonate.**—The deca-hydrate forms large transparent crystals which effloresce easily, passing over into the monohydrate. This, in turn, in very dry air or at a higher temperature loses water and becomes anhydrous.

Anhydrous sodium carbonate is a white opaque substance. It dissolves in water with the evolution of heat. A solution of sodium carbonate is fairly alkaline, due to hydrolysis since carbonic acid is a weak acid. For solutions of ordinary concentration, something like 1 to 2 per cent. of the carbonate is hydrolyzed.

**Uses of Sodium Carbonate.**—Sodium carbonate is used in making glass, soap, in the softening of water, in washing and bleaching of linen and cotton fabrics, washing wool, paper making, dyeing and dye manufacture, the making of sodium salts, as a reagent in the laboratory to furnish the carbonate ion, and for many other important and useful purposes. Its consumption amounts to millions of tons yearly.

**Sodium Bicarbonate.**—Sodium bicarbonate,  $\text{NaHCO}_3$ , which is also called sodium acid carbonate, sodium hydrogen carbonate, primary sodium carbonate, monosodium carbonate, baking soda, saleratus, or by the housewife simply soda, occurs in nature along with sodium carbonate. It is obtained in the manufacture of sodium carbonate by the Solvay process or by acting upon the monohydrate with carbon dioxide.

It is a white crystalline powder which decomposes into sodium carbonate, water, and carbon dioxide, when heated to a moderate temperature. A solution of the bicarbonate contains a little carbonic acid formed according to the following equation.



When the solution is boiled, the carbonic acid breaks down into water and carbon dioxide, which escapes in the form of bubbles.

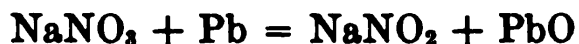
**Sodium Nitrate.**—Sodium nitrate,  $\text{NaNO}_3$ , occurs widely distributed in nature in small amounts and is found in enormous quantities in certain deposits in the desert regions of Chile. These deposits are scattered over an area a few miles in width and 500 miles long. The crude nitrate always contains considerable sodium chloride, nitrate and perchlorate of potassium, and sodium iodate, with occasionally some chromate. The iodine is an important by-product. The nitrate is purified by dissolving it out of the crude material with hot water and allowing the solution to crystallize.

The yearly production is about 2,000,000 tons which is something like 1 per cent. of the available supply.

Sodium nitrate crystallizes in rhombohedra which melt without decomposition at  $317^\circ$ . It is very soluble in water and deliquesces, which makes it unfit for the better grades of gunpowder. It is used in the manufacture of blasting powder, of nitric and sulfuric acids, of potassium nitrate, as a preservative

for meats, and in making sodium nitrite, but the greater part is used as a nitrogen fertilizer.

**Sodium Nitrite.**—Sodium nitrite,  $\text{NaNO}_2$ , is made by heating sodium nitrate with lead or iron and recrystallizing the product,



It is very soluble in water though less so than the corresponding potassium salt. It is largely used in the manufacture of organic dyes.

**Sodium Sulfate.**—Sodium sulfate, deca-hydrate,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  has been known for centuries under the name of Glauber's salts, having been first described by Glauber in 1658. The salt may also be obtained as the hepta-hydrate,  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$  and in the anhydrous state.

As has been mentioned, sodium sulfate is made as the first step in the Le Blanc process for the preparation of sodium carbonate and also for use in the manufacture of glass.

The solubility relations between the different forms of sodium sulfate are interesting and instructive, being in many ways typical of all salts which crystallize with different numbers of molecules of water of crystallization.

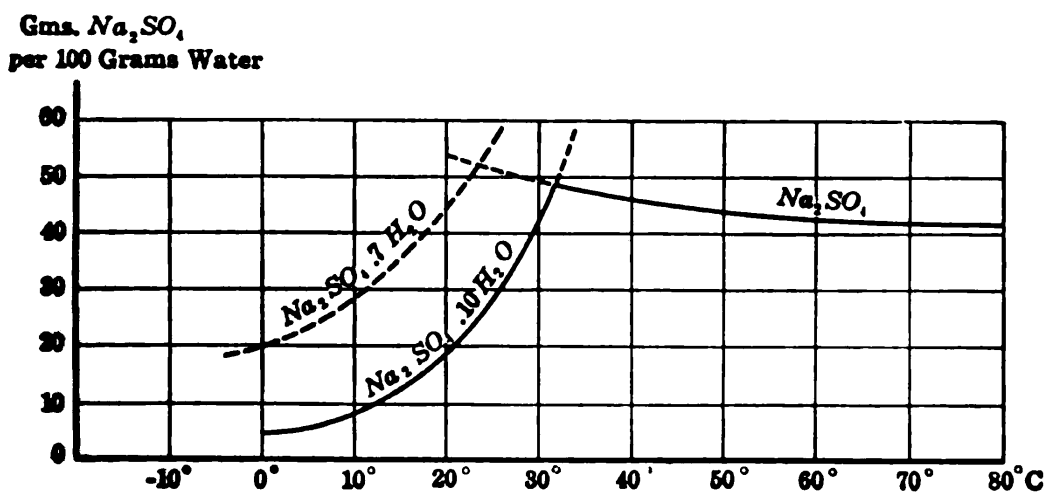


FIG. 54.

The two hydrates and the anhydrous salt are each distinct substances and as such, each has its own solubility at any given temperature, which, in general, is different from that of either of the others, as is shown by the curves in Fig. 54.

These curves show, for example, that at 20° a solution in

equilibrium with  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  will contain per 100 grm. of water 19.4 grm. of the salt calculated as  $\text{Na}_2\text{SO}_4$ , while those in equilibrium with  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$  or with the anhydrous salt contain respectively 44 grm. and 54 grm. of  $\text{Na}_2\text{SO}_4$  per 100 grm. of water. These figures demonstrate that the solubility of a salt cannot be expressed by a definite number unless there is given, in addition to the temperature and pressure at which the measurement is made, the particular solid phase with respect to which the solution is in equilibrium.

Sodium sulfate is especially prone to form supersaturated solutions and, if a solution be prepared which is saturated or nearly saturated with the salt at about  $32^\circ$ , but which does not contain the smallest trace of the solid deca-hydrate, be cooled to ordinary temperatures in a flask closed with a plug of cotton all the salt will remain in solution, although it contains about twice the solute which a saturated solution of the deca-hydrate would contain. If now even a very small piece of a crystal of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  be introduced into the liquid, crystallization will at once take place and continue until the solution is no more than saturated. Sodium sulfate is such a common substance that it is almost universally present in dust and the cotton plug is used to exclude the latter, and so prevent the crystallization of the salt.

The solubility curves for the deca-hydrate and the anhydrous salt intersect at  $32.4^\circ$  and hence at this temperature the two salts are in equilibrium and have the same solubility. At all temperatures below this point the anhydrous salt is the more soluble and is meta-stable toward the deca-hydrate, while above this point the deca-hydrate is the more soluble and is meta-stable. In the curves, meta-stable equilibrium is shown by the dotted and the stable by the solid lines.

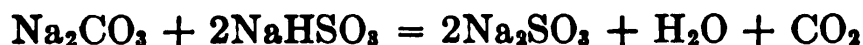
When crystals of the deca-hydrate are heated to  $32.4^\circ$ , they partially liquefy depositing some anhydrous salt and forming a solution saturated both with the deca-hydrate, and the anhydrous salt. The crystals of the deca-hydrate give a rather high vapor pressure of water and hence effloresce easily upon exposure to the air.

Sodium sulfate is used in medicine as a cathartic and also in the manufacture of glass and of sodium carbonate.

**Sodium Sulfit.**—Sodium sulfite,  $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ , is prepared by dividing a solution of sodium carbonate into two equal parts and saturating one with sulfur dioxide when carbon dioxide and acid sodium sulfite will be formed,



The remainder of the carbonate solution is then added and carbon dioxide and the neutral sulfite will be produced,



In addition to the acid and neutral salts mentioned above, a compound having the formula,  $\text{Na}_2\text{S}_2\text{O}_5$ , known as sodium disulfite or sodium meta-bisulfite is made in rather large quantities for use in photography, as is also the neutral sulfite.

When exposed to the air, the sulfites take up oxygen and are changed to sulfates. This process is generally retarded by the presence of small quantities of certain organic substances such as alcohol or sugar which here act as negative catalyzers. The use of the sulfites in photography depends largely upon their power of reacting with oxygen since they are added to the "developers," which are strong reducing agents to protect them from the oxidizing action of the air.

Sodium sulfite is also used as an antiseptic or preservative and as an "antichlor" to reduce any chlorine which may be left in the goods after bleaching with this substance.

**Sodium Sulfide.**—Sodium sulfide,  $\text{Na}_2\text{S}$ , is prepared on a large scale by the reduction of the sulfate with powdered coal at a high temperature as was done in the preparation of sodium carbonate by the Le Blanc process. It dissolves in water and the solution has an alkaline reaction owing to hydrolysis which results in the formation of some of the hydrosulfide,  $\text{NaHS}$ , or rather of the hydrosulfide ion,  $\text{HS}^-$ . The salt crystallizes with nine molecules of water as  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ , and is able to take up sulfur to form various polysulfides of which the compounds  $\text{Na}_4\text{S}_9 \cdot 14\text{H}_2\text{O}$ , and  $\text{Na}_2\text{S}_8$  are the best known.

Small quantities of these sulfides are used in the laboratory as reagents, but the salts find extensive use in the manufacture of some kinds of glass and in the removal of hair from hides.

**Sodium Thiosulfate.**—Sodium thiosulfate,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , is an important salt which may be made by boiling a solution of the sulfite with sulfur. The latter is taken up much as oxygen is by the sulfites, and thiosulfates are regarded as sulfates in which one atomic weight of sulfur has taken the place of an atomic weight of oxygen. The salt is obtained as a by-product of the Le Blanc process. The residue of calcium sulfide left in this process slowly oxidizes in the air to the thiosulfate, and when this is treated with sodium carbonate, calcium carbonate and sodium thiosulfate result.

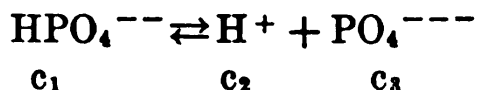
The penta-hydrate is very soluble and readily forms supersaturated solutions. It melts at  $48^\circ$  and if protected from dust will remain liquid at ordinary temperatures until brought in contact with some of the solid salt. This liquid may be regarded as either the supercooled hydrate or supersaturated solution.

The salt is used as an "antichlor" to destroy the excess of chlorine used in bleaching and as a protection against the "war gas" which is chlorine, and also as a fixing agent in photography, a use which will be discussed in connection with the silver salts.

**Oxyhalogen Compounds of Sodium.**—The methods of preparation, properties, and uses of sodium hydrochlorite,  $\text{NaClO}$ , and chlorate,  $\text{NaClO}_3$ , have already been given under the oxygen compounds of chlorine and will not be repeated here.

**Sodium Phosphates.**—Three sodium salts of orthophosphoric acid are known, monosodium phosphate,  $\text{NaH}_2\text{PO}_4$ , disodium phosphate,  $\text{Na}_2\text{HPO}_4$ , and trisodium phosphate,  $\text{Na}_3\text{PO}_4$ . The disodium salt,  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ , is the most familiar of these. It is made by neutralizing a solution of phosphoric acid with sodium hydroxide or carbonate and allowing it to crystallize. The salt is easily soluble and effloresces readily. It is used in medicine as a laxative and in the laboratory as a soluble phosphate reagent to furnish the hydrophosphate  $\text{HPO}_4^{--}$ , and the phosphate,  $\text{PO}_4^{---}$ , ions. Solutions of  $\text{Na}_2\text{HPO}_4$  are practically neutral in reaction, from which it follows that the ion  $\text{HPO}_4^{--}$  is but very slightly dissociated into the hydrogen and phosphate ions, so that the concentration of the latter is very small. For this reason, if the solution is to be used as a source of the phosphate ion,  $\text{PO}_4^{---}$ , sodium or ammonium hydroxide is added to

reduce the concentration of the hydrogen ion and so make the  $\text{HPO}_4^{--}$  ion break up. The reaction,



is reversible and according to the law of mass action,  $c_3 c_2 / c_1 = a$  constant. The addition of a base to the solution will decrease the concentration of the hydrogen ion and with it the product of  $c_2$  and  $c_3$  and this will of course have to be followed by a decrease in  $c_1$ , the concentration of the hydrophosphate ion. But the hydrophosphate ion decreases in concentration by changing into the hydrogen ion, which is used up by the base, and the phosphate ion which accumulates in the solution. So a solution of disodium phosphate to which sodium or ammonium hydroxide has been added contains a much larger amount of the phosphate ion than a pure solution of the salt and is used when the properties of the phosphate ion are sought.

The trisodium salt,  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ , is made by adding an excess of sodium hydroxide to a solution of the disodium salt and evaporating to crystallization. Its solution in water is very alkaline and the salt is practically completely hydrolyzed into  $\text{Na}_2\text{HPO}_4$  and  $\text{NaOH}$ . It is used to soften or break "hard water." It does this by precipitating the calcium and magnesium of the water as phosphates.

The monosodium salt is very soluble in water and the solution is acid toward litmus.

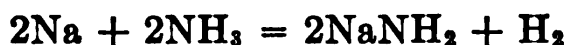
The sodium salts of the other phosphoric acids are not of much importance, except perhaps the metaphosphate,  $\text{NaPO}_3$ , which fuses easily and in this state dissolves many oxides and then solidifies to glass-like masses having characteristic colors. For this reason it is used in blowpipe analysis.

**Sodium Tetraborate.**—Borax or sodium tetraborate,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , has been described under boric acid (see p. 261). Like the metaphosphate, when melted it dissolves metallic oxides, and gives characteristically colored glass-like substances. Because of this, it is used in blowpipe analysis. It is also used as a flux in hard soldering.

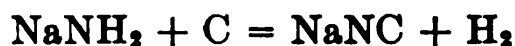
**Sodium Silicate.**—A salt having the composition  $\text{Na}_2\text{SiO}_3$  can be made by fusing together sodium carbonate and silicon dioxide.

It is soluble in water and is called water glass. It is used in fire proofing wood, in making a kind of artificial stone or sand brick, being mixed with sand and lime for this purpose, and in the household for preserving eggs.

**Sodium Cyanide.**—Sodium cyanide,  $\text{NaNC}$ , is made on a large scale for use in the extraction of gold, for which purpose it has some advantages over potassium cyanide; since a given weight of sodium cyanide has in it a larger amount of cyanogen, the essential ion for the purpose, than the same weight of potassium cyanide. The salt is made by passing ammonia over metallic sodium heated to  $300^{\circ}$  to  $400^{\circ}$  in an iron vessel when sodium amide,  $\text{NaNH}_2$ , is formed,



This sodium amide is then brought in contact with charcoal heated to dull redness when sodium cyanide and hydrogen are produced,



Sodium cyanide is also made by fusing the mixture of calcium cyanamide and carbon obtained by heating calcium carbide, in an atmosphere of nitrogen with sodium carbonate.



Like all other soluble cyanides, sodium cyanide is very poisonous.

**Sodium Acetate.**—Sodium acetate,  $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ , is a very easily soluble salt which is made by neutralizing acetic acid with sodium carbonate. It is used in the laboratory to decrease the acidity of a solution without making it neutral or alkaline. This is useful in analytical chemistry because of the fact that many precipitates will form in weakly acid solutions which are soluble in more highly acid solutions. To make the conditions favorable for the formation of such a precipitate in a solution which contains a strong acid, such as hydrochloric, all that is necessary is to add to the solution sodium acetate in sufficient quantity. The greater part of the hydrogen ion from the strong acid combines with the acetate ion to form undissociated acetic acid, because acetic acid is a weak acid and thus the acidity of the solution is decreased.

**Analytical Properties of Sodium.**—Like the salts of all other metals, the solutions of sodium salts show one set of properties in common, and this is really what is meant when it is said that they contain sodium as ion. In general, the statement of the analytical properties of an ion consists in giving a list of the more common ions with which it will form difficultly soluble compounds. There is, however, no very difficultly soluble compound of sodium, so this element must be recognized in some other way. For this, advantage is taken of the fact that the colorless flame of the Bunsen burner is colored intensely yellow by very small quantities of sodium and when this flame is viewed through a spectroscope, two bright yellow lines are seen if the instrument is very powerful or the two may appear as one in the smaller instruments (see Frontispiece). This is an exceedingly delicate test and will detect 0.0000000003 grm. of sodium. Enough sodium is present in practically all substances to give this test and one must judge as to whether sodium is present as an inconsiderable trace or as an essential constituent from the length of time which the flame color lasts as well as its intensity.

When the light from a powerful arc lamp is examined with a spectroscope a very bright continuous spectrum is seen. If the light from the arc passes through a Bunsen burner flame colored yellow by a sodium compound before it enters the spectroscope, black lines appear in exactly the position of the bright sodium lines when viewed in the absence of the arc light. In fact, the black lines may be made to change into bright ones simply by diminishing the intensity of the arc. This and other similar experiments lead to the conclusion that an incandescent gas will take up from a more intense source of light just that kind of light which it gives out, and when the more intense source of light is a solid, this will produce dark lines on a bright background. The dark lines come just where the incandescent gas alone would give bright lines. The solar spectrum consists of a bright background crossed by a very great number of dark lines many of which are identical in position with bright lines given by terrestrial substances when in the incandescent gaseous state. From these facts it is supposed that the sun consists of an intensely heated core surrounded by an atmosphere of gases which while incandescent are much cooler than the core and which con-

tain many of our well-known terrestrial elements. The presence of sodium for example, is clearly indicated by the fact that there are dark lines in the solar spectrum which exactly coincide with the bright lines of the sodium flame (see Frontispiece).

In this way the presence of something like forty terrestrial elements in the sun has been ascertained. Among these may be mentioned hydrogen, helium (first discovered in the sun and then found in the earth), calcium, carbon, chromium, cobalt, iron, magnesium, manganese, nickel, silver, sodium, potassium, and vanadium.

### POTASSIUM

**Occurrence.**—Potassium is never found free in nature, but occurs widely distributed in small quantities in the silicate rocks which compose the greater part of the earth's crust. On an average, potassium constitutes about 2.46 per cent. of the lithosphere. This is the same as the sodium content of the rocks. The silicates when acted upon by water and carbon dioxide slowly decompose and their potassium and sodium content passes into solution. One would expect then that the rivers flowing down into the sea would carry approximately equal quantities of sodium and potassium salts, but this is not the case, since the sodium greatly predominates. The explanation for this is found in the fact that soils have the power to hold back the potassium salts by what is known as adsorption (see p. 228).

Potassium salts are adsorbed by the soils while the sodium salts are not, and hence the latter easily find their way to the ocean. Because of this, the ocean contains relatively more of sodium salts than of potassium (see p. 274).

In spite of this disproportion between the sodium and potassium content of the ocean, it might be expected that the conditions which would give rise to the great deposits of salt would produce smaller deposits of potassium compounds. But since the potassium content of the sea is so small in comparison with that of the sodium, the ancient seas would have had to become nearly completely dry before any potassium salts would be deposited. This would put such salts at the very top of the deposits where they would be extremely liable to be dissolved and

washed away. So far as can be reasoned out from our present conditions, such deposits could only be formed when a great body of sea water dried up completely in a desert region and the deposits became covered so deep by dirt blown in from the surroundings that they were protected from any further action of water. At any rate the condition would be quite exceptional, and as a matter of fact only three large deposits of potassium salts are known; that in the neighborhood of Stassfurt, Germany, a smaller one at Kalusz in Austria, and another in northeastern Spain near Barcelona. The climate of these regions is now far from that of a desert, but there is some evidence that it was such at the time of the formation of the deposits. The discovery of beds of potassium salts in this country has frequently been reported of late, one of the most promising being that at Searles Lake in California and another the deposits of basic alum called alunite in Utah.

**Potassium Compounds and Plants.**—Growing plants seem to have an imperative need for compounds of the alkali metals, potassium and sodium. Those which grow on the land take up potassium compounds from the soil to such an extent that their ashes formerly constituted the chief source of these compounds. The plants growing in the sea and many of those along the seashore are rich in sodium salts. Some sea plants, however, notably the giant kelps of the Pacific, take up potassium compounds in such quantities that they may become an important factor in meeting the needs of this country for these very important substances. Large plants for the commercial extraction of potash salts from kelp are now being put in operation.

There is then a direct connection between the soluble potassium content of a soil and its fertility, for, of course, plants can only feed upon soluble substances. The soils usually contain large amounts of insoluble potassium compounds chiefly silicates, which slowly decompose under the action of the water and carbon dioxide, giving rise to soluble potassium salts and thus tending to keep up the supply of the latter in the soil. But if the land is kept under cultivation and the greater part of the crop removed as is often the case, soluble potassium compounds cannot be formed as rapidly as they are needed, and the fertility of the soil must decrease. The remedy is obviously to restore everything

possible to the soil, and to make up the deficiency in potassium by use of some of the potassium salts as fertilizers.

Animals have need for considerable quantities of sodium compounds chiefly for the chloride which constitutes the greater part of the salts in the body fluids, but their demand for potassium is rather small. Herbivorous animals get with their food much larger quantities of potassium and smaller quantities of sodium than they need. Now the elimination of the unnecessary potassium seems to be unavoidably accompanied by the excretion of the useful sodium compounds, and this accounts for the great appetite for sodium chloride shown by herbivorous animals. Carnivorous animals get their sodium and potassium in the proper proportions in their food and hence do not care especially for salt.

**Preparation of the Element.**—Metallic potassium was first prepared by Davy 1807. It is made by the same method that was used in the preparation of sodium, the electrolysis of the fused hydroxide. The demand for potassium is not large and only small quantities are made, because sodium which is much cheaper, will do nearly everything that potassium can do, and since the atomic weight of potassium is 39.1 while that of sodium is 23, 39.1 parts of potassium would be required to do the work which would be done by 23 parts of sodium at a much lower cost.

**Physical Properties.**—Potassium is a silver white metal which very quickly tarnishes upon exposure to moist air. It is waxy at ordinary temperatures, melts at  $62.5^{\circ}$  and boils at  $758^{\circ}$ ; the vapor is blue in color and the molecular weight is apparently identical with the atomic weight, 39.1. Potassium easily forms an alloy with mercury which is much like the corresponding sodium amalgam.

Sodium and potassium form an alloy which is interesting because, if it does not contain too much sodium, it is a liquid at ordinary temperatures.

**Chemical Properties.**—The chemical properties of potassium are practically the same as those of sodium except that potassium is somewhat more active, so that when thrown upon water the potassium gets hot enough to set fire to the hydrogen which is evolved and which burns with a violet flame, this being the color given to flames by potassium compounds.

In fact, the entire chemistry of potassium is so similar to that

of sodium that in most cases it will be necessary to add to what was given under sodium merely the slight points of difference presented by the potassium compounds.

**Potassium Hydride.**—Potassium hydride,  $\text{KH}$ , is prepared in the same way as the sodium hydride and is very similar to it in its properties.

**Potassium Oxides.**—Potassium forms two compounds with oxygen, a monoxide,  $\text{K}_2\text{O}$ , which dissolves in water to give potassium hydroxide and a peroxide,  $\text{K}_2\text{O}_2$ , which differs from the peroxide of sodium in composition, but like it, dissolves in water with the formation of the hydroxide, hydrogen peroxide and oxygen.

**Potassium Hydroxide.**—Potassium hydroxide,  $\text{KOH}$ , or caustic potash is so similar to sodium hydroxide that practically everything which was said concerning that compound might be repeated here as a description of potassium hydroxide. It may be prepared by the electrolysis of potassium chloride or by acting upon a dilute boiling solution of the carbonate with calcium hydroxide (milk of lime), calcium carbonate being precipitated and potassium hydroxide left in solution. It is exceedingly soluble.

It is a very strong base and is used as such, but wherever possible sodium hydroxide is used in its place. The reason for this is that the sodium hydroxide is cheaper and less of it is required to do a given amount of chemical work because of the smaller atomic weight of sodium.

Potassium hydroxide is very deliquescent, and its solutions take carbon dioxide from the air forming the carbonate which is also deliquescent.

The chief technical use for potassium hydroxide is in the manufacture of soft soap and of oxalic acid.

**Potassium Chloride.**—Potassium chloride,  $\text{KCl}$ , is found in the potassium deposits of Stassfurt and is known as sylvite. It is also found there as double salts with magnesium chloride,  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , known as carnallite and with magnesium sulfate,  $\text{MgSO}_4 \cdot \text{KCl} \cdot 3\text{H}_2\text{O}$ , kainite. The greater part of the potassium chloride of commerce is made from carnallite. The crude carnallite is crushed and heated with a solution of magnesium chloride left from previous operations. In this the carnallite

giving oxygen as one of its products. It was used by Scheele as one of the sources of this substance at the time of his discovery of the element.

Potassium nitrate is used in the laboratory, in medicine, in preserving meats to which it imparts a red color, and in the manufacture of fireworks and gunpowder. This last use absorbs by far the greater part of the  $\text{KNO}_3$  of commerce.

The composition of gunpowder varies somewhat but is near 75 per cent. potassium nitrate, 10 per cent. sulfur, 14 per cent.

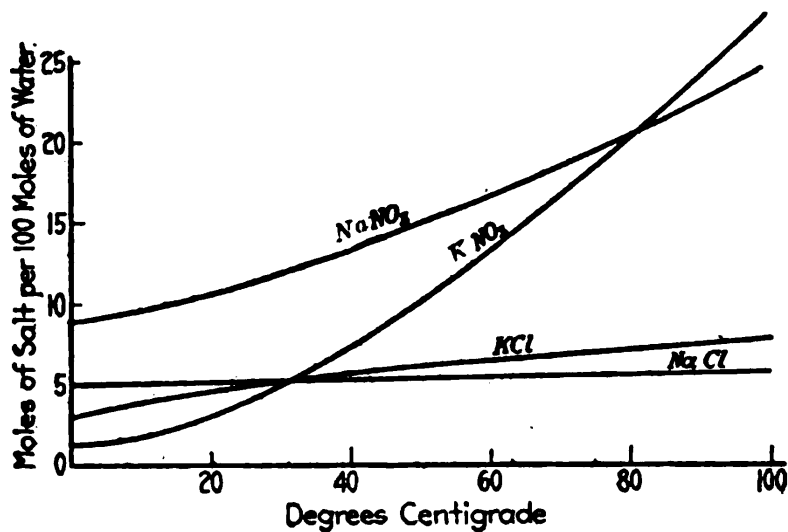


FIG. 55.

charcoal, and 1 per cent. water. The solid ingredients are pulverized separately, mixed together, moistened and ground until thoroughly incorporated. The mixture is then subjected to great pressure and afterward broken up into fragments which are sorted into sizes by sifting. The grains are polished or given a glaze by rattling them in a barrel, dried to remove the water added during the various operations, and finally dusted by passing the powder over very fine sieves.

Gunpowder contains two easily combustible substances, sulfur and charcoal in intimate contact with a very good oxidizing agent, potassium nitrate. At a somewhat elevated temperature, these react very rapidly with the production of the gases nitrogen, carbon monoxide, carbon dioxide, hydrogen, marsh gas, hydrogen sulfide and a number of solid substances chief among which is potassium carbonate. The great amount of gas produced together with the high temperature of the reaction, about  $2,200^{\circ}\text{C}$ ., produces great pressure which would reach above 6,400

atmospheres or 47 tons per square inch if the products of the explosion occupied the volume of the gunpowder before the explosion. To this high pressure the well-known effects of gunpowder are due.

Sodium nitrate is much cheaper than the potassium salt, and is used in making the lower grades of powder for blasting, but cannot be used in the better kinds because it is deliquescent.

**Potassium Carbonate.**—Potassium carbonate,  $K_2CO_3$ , which is called potash or pearlash was formerly the most important of the potassium salts as it was the source of other potassium compounds, but since the discovery of the Stassfurt deposits it has largely lost its position. In former times, it was obtained from wood ashes by leaching them, using the principle of counter currents, but it is now chiefly obtained from the potassium sulfate of the Stassfurt deposits by a modification of the Le Blanc process for the preparation of soda; or from potassium chloride by taking advantage of the fact that when carbon dioxide under pressure is passed into potassium chloride solution containing magnesium carbonate in suspension, a double salt having the formula  $KHCO_3 \cdot MgCO_3 \cdot 4H_2O$  is deposited at temperatures below  $24^\circ C$ . This salt is decomposed by hot water, forming  $MgCO_3$  which is precipitated, carbon dioxide which passes out of the solution, and a solution of potassium carbonate from which the salt may be obtained.

Potassium carbonate is also obtained from the residue of beet sugar manufacture, and some is still extracted from wood ashes.

Potassium carbonate is a white solid; it is deliquescent and hence is very soluble in water. The solution is alkaline in reaction because of hydrolysis and the formation of  $HCO_3^- + OH^-$ .

It is used in making soft soaps, hard glass, and for the preparation of other potassium salts.

**Potassium Bicarbonate.**—Potassium bicarbonate,  $KHCO_3$ , potassium acid carbonate or primary potassium carbonate as it is called, like the corresponding sodium compound, is much less soluble than the normal carbonate and may be prepared by passing carbon dioxide through a strong solution of the carbonate.

**Potassium Cyanide.**—Potassium cyanide,  $KNC$ , is an important salt which is manufactured by heating potassium

ferrocyanide,  $\text{K}_4\text{Fe}(\text{NC})_6$ , with potassium carbonate when the following reaction takes place,



The salt KNCO is potassium cyanate and cannot be easily separated from the cyanide. If the ferrocyanide is heated alone, carbide of iron and nitrogen are formed besides the potassium cyanide. This process gives pure KNC but wastes cyanogen. By heating a mixture of dry potassium ferrocyanide with sodium, a mixture of potassium and sodium cyanides is obtained which is as good for most purposes as potassium cyanide and is sold as such. The equation is,



Potassium cyanide is now made by the action of ammonia upon a fused mixture of potassium carbonate and charcoal. The reaction is apparently much like that for the preparation of sodium cyanide from the metal, ammonia and charcoal; for metallic potassium may be formed by the action of carbon on the carbonate.

Potassium cyanide is very soluble in water and the solution is intensely and very rapidly poisonous. Hydrocyanic acid is a very weak acid, so solutions of potassium cyanide react alkaline owing to hydrolysis. The hydrocyanic acid formed can be readily detected by its odor.

Potassium cyanide is used in large quantities in gold mining and in electroplating with gold and silver. It is used in the laboratory wherever a solution containing the cyanogen ion is required and also as a reducing agent. When it acts in the latter capacity, potassium cyanate KNCO is formed. When heated with sulfur, the latter is taken up forming a thio compound analogous to the cyanates, known as potassium thiocyanate, KNCS, which is used in analytical work. This salt is sometimes, though incorrectly, called potassium sulphocyanide.

**Potassium Sulfate.**—Potassium sulfate occurs in nature in schoenite  $\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  and several other Stassfurt salts. It is obtained from schoenite by adding potassium chloride and a little water, on heating, the comparatively difficultly soluble

potassium sulfate crystallizes out and magnesium chloride is left in solution.

It is used in the preparation of potassium carbonate and of alum,  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  but chiefly as a fertilizer.

**Analytical Properties of Potassium.**—Solutions of potassium salt all have certain properties in common which are expressed by saying that they contain potassium as ion.

Potassium compounds impart to the flame of the Bunsen burner a violet coloration which is easily masked by a little sodium unless the flame is viewed through a blue glass which cuts off the yellow sodium light and allows the violet of the potassium to be seen. The spectrum of potassium consists of a fairly strong line toward the extreme red end of the spectrum, a much fainter red line near the orange and a weak line well out in the violet end of the spectrum. In between these lines is a host of faint ones so close together that in the smaller instruments they are not seen separately, but appear as a band of light from the orange to the violet (see Frontispiece). None of the potassium lines is anywhere near as intense as the sodium line and hence the spectroscopic test for potassium is far less delicate than that for sodium.

Potassium in the ionic condition differs from sodium in that it will combine with a number of different ions to form compounds which are sufficiently difficultly soluble in water to make them useful for the detection and determination of this element. Naturally for such a purpose the less soluble a salt the more useful it is, since the delicacy of the test and the accuracy of the determination depend directly upon this property.

Potassium cobaltinitrite,  $\text{K}_3\text{Co}(\text{NO}_2)_6$ , is the least soluble of the potassium salts, and is thrown down as a yellow precipitate when a solution of sodium cobaltinitrite,  $\text{Na}_3\text{Co}(\text{NO}_2)_6$ , which contains the cobaltinitrite ion  $\text{Co}(\text{NO}_2)_6^{--}$  is added to a neutral or slightly acid solution of a potassium salt, unless the latter be very dilute. This is a sensitive test for potassium, but is not as characteristic as the spectrum since ammonium, rubidium, and cesium compounds give very similar precipitates with the cobaltinitrite. But ammonium compounds are easily removed and rubidium and cesium occur so rarely that practically the test is a very good one for potassium.

Potassium cobaltinitrite has a small but definite solubility

which is diminished by the presence of an excess of either potassium or of cobaltinitrite as ion. In fact, it is a general rule that the solubility of a salt is diminished by increasing the concentration of one of its component ions.

Potassium as ion will also give rather difficultly soluble precipitates with picric acid,  $C_6H_2(NO_2)_3OH$ , perchloric acid,  $HClO_4$ , hydrofluosilicic acid,  $H_2SiF_6$ , chloroplatinic acid,  $H_2PtCl_6$ , and tartaric acid,  $H_2C_4H_4O_6$ , the precipitates being potassium picrate,  $C_6H_2(NO_2)_3OK$ , potassium perchlorate  $KClO_4$ , potassium fluosilicate,  $K_2SiF_6$ , or potassium hydrogen tartrate  $KHC_4H_4O_6$ . The conditions which affect the solubility of this latter compound are so typical of those of other compounds that they are worthy of a careful study.

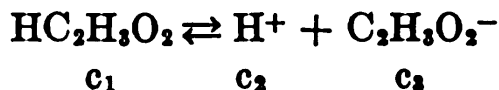
When a strong solution of tartaric acid is added to a rather concentrated solution of a potassium salt, say the chloride or nitrate, the solution becomes supersaturated with respect to potassium hydrogen tartrate,  $KHC_4H_4O_6$ . This supersaturation may be so great that the solution will spontaneously deposit crystals, or it may persist until the solution is shaken vigorously or until a minute crystal of the salt is added. Of course after crystallization has once started it will continue until the solution becomes exactly saturated with the salt. After this point has been reached the addition of various reagents will produce interesting changes in the solubility of the substance. For example, the addition of a few drops of sodium hydroxide solution will cause a marked increase in the quantity of precipitate showing that the solubility of the potassium hydrogen tartrate has been decreased, but the addition of an excess of sodium hydroxide will cause the entire precipitate to disappear showing that an excess of this reagent increases the solubility of the potassium salt.

Further, the addition of either sodium acetate or of a very soluble potassium salt will decrease the solubility of the hydrogen tartrate, and cause a marked increase in the quantity of precipitate formed in the solution described above.

The addition of a very moderate amount of one of the stronger acids such as hydrochloric, nitric, or sulfuric to a solution containing a precipitate of potassium hydrogen tartrate will increase the solubility of the latter and cause the precipitate to disappear.

acetic acid on the other hand has but little effect. Tartaric acid is a weak acid and this behavior of its potassium salt is typical of all difficultly soluble salts of weak acids, so that a general law may be put forward which says: *The difficultly soluble salts of weak acids dissolve upon the addition of stronger acids.* The converse of this is not true, the difficultly soluble salts of strong acids are not dissolved by weak acids nor are they, as a rule, dissolved by strong acids.

Various more or less satisfactory explanations for these phenomena may be given, but the most useful and instructive is that offered by a combination of the theory of electrolytic dissociation with the law of mass action. According to the theory, an electrolyte in solution is partially broken up into ions as shown below for acetic acid,

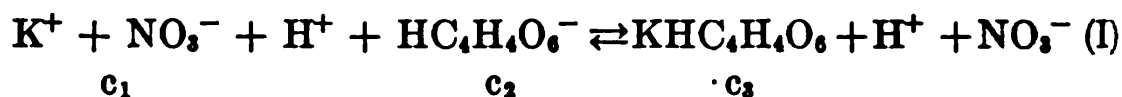


This is to be regarded as a reversible reaction and so subject to the law of mass action. Hence if  $c_1$  represents the concentration of the undissociated acetic acid and  $c_2$  and  $c_3$  that of the hydrogen and acetate ions respectively, equilibrium will result when,

$$\frac{c_2 c_3}{c_1} = K$$

If this be tested by experiment, the various concentrations being calculated from the electrical conductivity of the solution, the result will be found to agree closely with the theory as expressed in the mathematical relation just given. This is true not only for acetic acid but also for all other weak acids and for weak bases. It is true too, for dilute solutions of the more highly dissociated substances, the strong acids and bases and the salts, but apparently does not hold for the more concentrated solutions of these substances. This may be due to the conductivity being an imperfect measure of the concentration of the ions in such solutions, or to some other influence being superimposed upon those which are measured. Fairly satisfactory explanations of these deviations can be given, but are not of interest at this point because these deviations from the simple theory and law given above are not such as would alter any conclusion which

we might reach as to the kind of change which would follow the addition of any given reagent, but would simply affect the calculation as to the extent of such change. For qualitative purposes, then, the theory of electrolytic dissociation and the law of mass action may be combined and treated as though they exactly describe the actions of the substances. With this as preliminary, the discussion of the action of the various reagents upon potassium hydrogen tartrate as precipitated from solutions of potassium nitrate by solution of tartaric acid may be taken up in detail. The equation for the main reaction and equilibrium is as follows:



The equilibrium here is between the potassium ion, the hydrogen tartrate ion, and the undissociated potassium hydrogen tartrate. The concentration of these substances being represented respectively by  $c_1$ ,  $c_2$ , and  $c_3$ , the mass law equation becomes,

$$\frac{c_3}{c_1 c_2} = K$$

It cannot be too strongly emphasized that  $c_3$  represents the concentration of that portion of the potassium hydrogen tartrate which, while undissociated, is actually present in the solution in the dissolved state. It does not in any way represent that which is present as a precipitate. The only connection between  $c_3$  and the precipitate is found in this, that when the solution is in equilibrium with some of the precipitate, *i.e.*, is saturated, the equilibrium will be between the undissociated  $KHC_4H_4O_6$  in solution and that in the precipitate; and in this case, as in all others where there is equilibrium between the same substance in two phases, the equilibrium is determined by the ratio of the concentration of the substance in the two phases and not by the absolute amount of either phase. Therefore, since the concentration of the  $KHC_4H_4O_6$  is fixed and constant in the solid phase,  $c_3$ , that of this substance in solution must be fixed and constant also. From which it would follow that the product of  $c_1$  times  $c_2$  would be constant for this saturated solution, and this point should be appreciated and kept thoroughly in mind.

In addition to equilibrium I, given above, there are two others which are of importance in this connection.



The condition for equilibrium being,  $\frac{c_5}{c_4 c_2} = K'$

and



Equilibrium resulting when,  $\frac{c_2}{c_4 c_6} = K''$

Now it must be remembered that all three of these equilibria are present at the same time in a solution which contains potassium nitrate and tartaric acid, and that anything which alters one changes each of the others.

The addition of a few drops of sodium hydroxide to the solution will affect first equation II by decreasing  $c_4$ , the concentration of the hydrogen ion, through the formation of water, but a decrease in  $c_4$  will be followed by a decrease in  $c_5$  and this will result in an increase in  $c_2$ . But  $c_2$  comes in the equilibrium I and its increase at once produces an increase in  $c_3$ . However, the solution was saturated with potassium hydrogen tartrate and hence the increase in  $c_3$  makes it supersaturated and results in the increase in the precipitate mentioned in the list of facts which were to be explained.

The action of sodium acetate can now be easily understood since it acts like the hydroxide to decrease the concentration of the hydrogen as ion.

An excess of sodium hydroxide, it will be recalled, redissolved the precipitate of potassium hydrogen tartrate; the explanation for this apparently contradictory behavior is as follows: As the hydroxide is added, water is formed decreasing  $c_4$  and causing the undissociated tartaric acid to break up as shown in II until all the tartaric acid is transformed then the further addition of hydroxide will result in the breaking up of the hydrotartrate  $\text{HC}_4\text{H}_4\text{O}_6^-$  as shown in equation III; so by decreasing  $c_4$  through the addition of NaOH,  $c_2$  will be first increased and then decreased. But

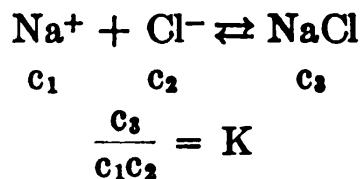
since  $c_2$  is one of the factors in equation I, a decrease in  $c_2$  will affect I, and will have to be followed by a decrease in  $c_3$ . But if  $c_3$  is decreased, the solution will become unsaturated and some of the precipitated substance will have to go into solution. So it may be easily seen why the solubility of potassium hydrogen tartrate is increased by the addition of an excess of sodium hydroxide.

The increase in solubility of  $\text{KHC}_4\text{H}_4\text{O}_6$  upon the addition of strong acids can be easily explained by considering the effect of the increase in the concentration of the hydrogen ion,  $c_4$ , upon II. If  $c_4$  is increased, to keep the fraction  $c_3/c_4c_2$  constant,  $c_3$  will have to increase which can only happen at the expense of  $c_2$ , so  $c_2$  will decrease. But in I a decrease in  $c_2$ , as we have seen, is followed by a decrease in  $c_3$  and this in turn by the solution of the precipitate. The failure of acetic acid to redissolve the precipitate can be understood, because acetic acid is so weak that it does not materially increase  $c_4$  and therefore does not decrease  $c_2$  and  $c_3$ , and hence leaves the solubility practically unaltered.

While potassium hydrogen tartrate is a fairly important substance, great quantities of it being used in the more expensive baking powders for example, it is not important enough to justify the time expended upon this discussion were it not for the fact that it is typical of most other substances, and that a thorough understanding of what is going on here will enable the student to deal easily with all other cases.

Under sodium chloride it was mentioned that this salt would be precipitated from its saturated solution by the addition of hydrogen chloride.

This may be understood by considering the following equilibrium:



If now hydrogen chloride be passed into the solution,  $c_2$  will be increased, and this will of necessity be followed by an increase in  $c_3$ , and a decrease in  $c_1$  to correspond; but an increase in  $c_3$  makes the solution supersaturated, and brings about the precipitation of the salt. A strong solution of hydrochloric acid may be used

instead of the gaseous hydrogen chloride with similar results. Potassium chloride will be precipitated in the same way and for the same reason by passing hydrogen chloride into its solution.

As was mentioned in the preliminary to this discussion, page 305, this simple form of mass law treatment does not take into account all the factors and hence does not quantitatively describe the complex phenomena present in these cases, but it does fit them and others qualitatively.

### RUBIDIUM AND CESIUM

The methods of spectroscopic analysis were developed by Bunsen and Kirchoff about 1859 to 1860 and were immediately utilized by them in a search for new elements. In this they were successful for in 1860 they announced the discovery of a new alkali metal whose spectrum was characterized by two bright blue lines and hence was named Cesium, Cs, from *cæsius*, the Latin word for the blue of the clear sky. Again, in 1861, they discovered another alkali metal whose spectrum consisted of two very strong lines in the violet and a number of others in the red, yellow and green portion of the spectrum. Two of the red lines are deeper red than the potassium lines, and hence the element was called Rubidium, Rb, from *rubidius* the Latin word for the darkest red color.

Rubidium and cesium are always found in connection with lithium, sodium, and potassium. They are so like one another and so very much like potassium that it is a difficult matter to separate them not only from each other but also from potassium.

Metallic rubidium and cesium may be obtained by heating their corresponding hydroxide with powdered magnesium.

Rubidium is a brilliant silver white metal which melts at  $38.5^{\circ}$  and boils at  $696^{\circ}$ . It has a density of 1.52 and acts upon water even more vigorously than potassium. The hydroxide so formed,  $\text{RbOH}$ , is at least as strong as that of potassium. The atomic weight of rubidium is 85.45.

Metallic cesium has a silver white color, melts at  $26.5^{\circ}$  and boils at  $670^{\circ}$ . Its density is 2.4. It is even more active chemically than rubidium. Cesium hydroxide,  $\text{CsOH}$ , is a very strong base, and its salts are isomorphous with those of potassium and rubidium. The atomic weight of cesium is 132.81.

Potassium, rubidium and cesium form a triplet of very closely related elements. The difference between the atomic weight of potassium, 39.1 and that of rubidium 85.45 is 46.35 which is just about that between rubidium and cesium which is 47.36. The same sort of relation exists between the triplet formed by chlorine, bromine, and iodine and here, too, the difference in atomic weight is about the same, being roughly 45. In a good many ways the properties of these three elements vary in a regular manner with the atomic weight as may be seen from the following table.

As the atomic weight of the metal increases.  
The chemical activity of the metal increases.  
The solubility of the hydrotartrate increases.  
The solubility of the sulfate increases.  
The solubility of the chloride increases.  
The solubility of the chlorplatinate decreases.  
The solubility of the alum decreases.  
The boiling and melting points of the metals decrease.

#### AMMONIUM

In the discussion of ammonia,  $\text{NH}_3$ , it was pointed out that this substance would combine directly with acids forming ammonium salts. For example, ammonium chloride,  $\text{NH}_4\text{Cl}$ , is formed by the union of ammonia and hydrogen chloride,



Ammonium chloride when dissolved acts as though it were dissociated into chlorine as ion and the complex cation  $\text{NH}_4^+$ , called the ammonium ion. This ion forms a long list of salts and is so very similar to potassium in its properties that it would be entirely out of place not to discuss it here in connection with this element. Most of the ammonium salts are isomorphous with the corresponding compounds of potassium, and the ammonium ion gives difficultly soluble compounds with the same reagents that the potassium ion does. So it is a rather easy matter to mistake the ammonium ion for the potassium.

The sources and methods of preparation of some of the ammonium compounds have already been mentioned in connec-

tion with the discussion of the compounds of nitrogen, pp. 193–194.

**Ammonium Hydroxide.**—Ammonium hydroxide is formed when ammonia dissolves in water, and may be obtained at low temperatures as a solid which melts at  $-79^{\circ}$ . Its solution shows comparatively weak basic properties indicating a small concentration of hydroxyl.

**Ammonium Chloride.**—Ammonium chloride or sal ammoniac,  $\text{NH}_4\text{Cl}$ , is one of the more important of the ammonium salts. It is easily soluble in water, and crystallizes in cubes or octahedra. Its solutions are slightly acid due to hydrolysis. When heated to about  $350^{\circ}$ , it decomposes into ammonia and hydrogen chloride which pass off as gases, and recombine when they reach a cooler place, forming ammonium chloride, hence ammonium chloride is volatile. Most other ammonium salts undergo similar decomposition when heated giving ammonia and the acid. It is used in making dry cells and some other kinds of electrical batteries, as a reagent in the laboratory, in soldering and in medicine. Some idea of the extent of the use of ammonium chloride in batteries may be gathered from the fact that 50,000,000 dry cells are made in this country every year.

**Ammonium Nitrate.**—Ammonium nitrate,  $\text{NH}_4\text{NO}_3$ , is a white crystalline salt. At temperatures somewhat higher than its melting-point,  $160^{\circ}$ , ammonium nitrate decomposes into nitrous oxide and water;



In this respect, it differs from most of the other ammonium salts since it does not yield ammonia and the acid. The difference is presumably due to the oxidizing action of the nitric acid on ammonia. The nitrous oxide is a powerful oxidizing agent; for this reason the nitrate is used in some explosives, in fact under exceptional conditions it is explosive without any admixture.

**Ammonium Sulfate.**—Ammonium sulfate,  $(\text{NH}_4)_2\text{SO}_4$ , is in some ways the most important of the ammonium salts. It is obtained in the recovery of ammonia in the gas works, and is the starting-point for the preparation of most of the ammonium compounds. It is extensively used for this purpose, but more

as a nitrogen fertilizer, something like 500,000 tons of it being used for agricultural purposes each year.

It is a white crystalline salt isomorphous with potassium sulfate.

**The Sulfides of Ammonia.**—Ammonium hydrosulfide,  $\text{NH}_4\text{HS}$ , is formed when equal volumes of ammonia and hydrogen sulfide are brought together. It is a crystalline substance which readily decomposes into its constituents.

The salt is easily soluble in water and gives the ammonium and hydrosulfide ions.

Two volumes of ammonia and one of hydrogen sulfide unite to form ammonium sulfide,  $(\text{NH}_4)_2\text{S}$ . This is much less stable than the acid salt and passes quickly into the latter with the loss of ammonia. When dissolved in water, it is largely hydrolyzed giving ammonium hydroxide and the hydrosulfide ion,  $\text{HS}^-$ .

Solutions of these salts may be made by passing hydrogen sulfide into ammonium hydroxide solution. They are used as reagents to furnish the sulfide ion  $\text{S}^{--}$  and hydrosulfide  $\text{HS}^-$  which are necessary for the precipitation of such sulfides as required a higher concentration of sulfur as ion than is furnished by hydrogen sulfide, the sulfides of manganese and zinc for example.

A solution of ammonium sulfide will dissolve sulfur, and thereby acquires a yellow color and is then known as yellow ammonium sulfide. It contains polysulfides and is used as a reagent.

**Ammonium Carbonate.**—When an excess of carbon dioxide is passed into a solution of ammonium hydroxide, ammonium bicarbonate,  $\text{NH}_4\text{HCO}_3$ , is formed.



This is a fairly stable white crystalline salt which is soluble in water. The solid has a slight odor of ammonia and tends to decompose into ammonia, water and carbon dioxide. This reaction is quite rapid at moderately elevated temperatures and is employed by bakers who use the bicarbonate as a leavening agent much as the housewife does baking powder. For this purpose, the bicarbonate has the distinct advantage over the

baking powder that it leaves practically no foreign substance in the food.

An excess of ammonium hydroxide will convert the bicarbonate into the carbonate,  $(\text{NH}_4)_2\text{CO}_3$ , but this is very unstable and soon decomposes.

Commercial ammonium carbonate is made by subliming a mixture of the sulfate and powdered calcium carbonate. It is a mixture of the bicarbonate and carbamate,  $\text{NH}_4\text{CO}_2\text{NH}_2$ . The latter is formed when ammonia combines with carbon dioxide.

**Ammonium Oxalate.**—Ammonium oxalate,  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  is made by neutralizing oxalic acid with ammonium hydroxide. It is a white crystalline salt soluble in water and much used as a reagent.

**Ammonium Thiocyanate.**—Ammonium thiocyanate,  $\text{NH}_4\text{NCS}$ , is very easily soluble in water and is exceedingly poisonous. It is much used as a reagent.

**Analytical Reactions of Ammonium.**—The ammonium ion forms difficultly soluble compounds with the cobaltinitrite, chloroplatinate, and hydrotartrate ions. These compounds cannot be distinguished by the eye from the corresponding potassium compounds. Ammonium compounds, however, do not give a flame test or spectrum when introduced in the Bunsen flame.

A very sensitive and characteristic test for ammonium compounds is based upon the fact that when a soluble base like sodium hydroxide is added to an ammonium salt, undissociated ammonium hydroxide is formed owing to the weakly basic character of this substance. As soon as the ammonium hydroxide is formed it breaks down into water and ammonia. The latter may be easily detected by its odor or by its action on moistened red litmus which is turned blue when held in the vapors over the solution. The equations for reactions in the solution are as follows.



The ammonia then vaporizes and dissolves in the water on the litmus where the following reactions take place



and it is this hydroxyl which turns the litmus blue.

Of course potassium compounds can do nothing like this so it is very easy in this way to distinguish between the two sets of compounds.

**Ammonium Amalgam.**—The great similarity between the ammonium ion and the potassium ion suggests that if free ammonium,  $\text{NH}_4$ , could be obtained it would be metallic in character. Attempts to prepare free ammonium have so far been unsuccessful, but an amalgam of this substance and mercury can be made either by electrolyzing most ammonium salts (the nitrate will not do), using a mercury cathode, or by the action of sodium amalgam on an ammonium salt solution.

Below  $-85^\circ$  the amalgam is a hard stable substance, but at ordinary temperatures it is very spongy and consists largely of a mass of bubbles due to the decomposition of the dissolved ammonium into hydrogen and ammonia. That ammonium has metallic characteristics is shown by the fact that it dissolves in mercury which will not dissolve anything else that is not a metal.

## LITHIUM

The element lithium is very widely distributed and is obtained from petalite,  $\text{LiAl}(\text{Si}_4\text{O}_{10})_2$ , and lepidolite or lithium mica. The metal is prepared by the electrolysis of the fused chloride. It is a solid with a silver white luster, melts at  $186^\circ$  and boils above  $1400^\circ$ . Its density is 0.594 so that it floats on the petroleum used for its preservation.

The atomic weight of lithium is 6.94 making it the third element in the order of atomic weights. It is active chemically but less so than the other members of the alkali group. It reacts rapidly with water but the metal does not melt and the hydrogen is not inflamed. It burns when heated in air, hydrogen, chlorine, bromine, iodine, sulfur, or nitrogen. This last property is interesting and somewhat important because there are not many things which will combine so readily with nitrogen. Lithium nitride,  $\text{Li}_3\text{N}$ , is formed.

Perhaps the most significant properties of lithium are that its phosphate,  $\text{Li}_3\text{PO}_4$ , and its carbonate,  $\text{Li}_2\text{CO}_3$ , are rather difficultly soluble in water, and that the bicarbonate  $\text{LiHCO}_3$  is more soluble than the carbonate. With every other alkali metal, the

bicarbonate is less soluble than the carbonate and the phosphate is easily soluble. The phosphates and carbonates of the members of the next group in the periodic system are difficultly soluble and the bicarbonates are more soluble than the corresponding carbonates. This shows that lithium has properties that make it a sort of connecting link or transition element between the two groups. That it really belongs to the alkali metals and not with the Group II is shown by the fact that it is monovalent while the members of Group II are divalent.

Beryllium, the first member of Group II, is like lithium in that it has properties which connect it with both Groups II and III.

In many ways it would have been more logical to have opened the discussion of the metals with that of lithium, but its postponement until this point just before taking up Group II is justified by the properties mentioned above.

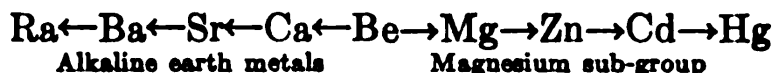
**Lithium Carbonate.**—Lithium carbonate  $\text{Li}_2\text{CO}_3$  is commercially the most important lithium salt. It is used in medicine and for the preparation of lithium salts.

**Lithium Chloride.**—Lithium chloride is used in making artificial mineral waters and for making red fire and other fireworks.

**Analytical Properties of Lithium.**—Lithium is very easily detected by the fact that it imparts a bright red color to the Bunsen flame and that its spectrum contains a very strong red line which is visible even when the lithium is present in exceedingly small quantities.

## CHAPTER XXII

### GROUP II



**General.**—The first member of Group II in the periodic system is beryllium. As mentioned under lithium, beryllium has properties which connect it both with Group II and with Group III and therefore its discussion will be postponed until a later point. The other members of the group fall naturally into two well-marked sub-groups; the one called the alkaline earth metals and comprising the common metals, calcium, strontium, and barium, and the very rare element radium; and the other sub-group called the magnesium family containing beryllium, magnesium, zinc, cadmium, and mercury. All the members of the group are divalent, but mercury also forms a series of compounds in which it is monovalent.

Calcium, strontium, and barium form a triplet of very closely related elements, and for a long time have been grouped together under the name of the alkaline earth metals. The discussion of the group will be opened with that of these metals since they are in many ways more closely connected with the alkali metals than are the members of the magnesium sub-group.

#### THE ALKALINE EARTH METALS

##### CALCIUM

The compounds of calcium have been known and used from the very earliest times, but the element itself was first prepared, although in an impure state, by Davy in 1808.

**Occurrence.**—Calcium compounds are very abundant and are widely distributed over the earth's surface in the form of silicates, carbonates (limestone), sulfates, fluoride, phosphates, borates,

etc. The element is present in the sun and certain of the fixed stars as shown by their spectra.

Compounds of calcium are indispensable for the growth and life of plants and animals. The bones and teeth of animals are composed largely of calcium phosphate but contain some carbonate and fluoride in addition.

**Preparation of the Element.**—Calcium is prepared on a fairly large scale by the electrolysis of the fused chloride, the anode, consisting of carbon and the cathode of an iron rod. The calcium, as it is liberated, clings to the end of the rod and the latter is gradually withdrawn from the fused salt, causing the calcium to build up an irregular cylinder of the metal. It is essential that the temperature of the fused calcium chloride be kept as low as possible; for this purpose, calcium fluoride is sometimes added to the bath, since it dissolves and lowers the melting-point of the chloride.

**Properties.**—Calcium is a silver white crystalline metal which melts at  $800^{\circ}$  and volatilizes below its melting-point in a vacuum. It has a density of 1.55 and is malleable, although somewhat harder than lead. It tarnishes rapidly in moist air at ordinary temperatures, but may be turned and polished in the air if kept hot.

Calcium decomposes water, forming hydrogen and calcium hydroxide,  $\text{Ca}(\text{OH})_2$ . It acts vigorously on acids. When heated in the air, it burns brilliantly and also combines rapidly at higher temperatures with nitrogen, chlorine, hydrogen, sulfur, silicon, and phosphorus. With nitrogen, calcium nitride,  $\text{Ca}_3\text{N}_2$ , is formed. When calcium is heated in a closed vessel, both the oxygen and nitrogen are removed and a very high vacuum results.

The atomic weight of calcium is 40.07.

**Calcium Hydride.**—Calcium combines directly with hydrogen to form calcium hydride,  $\text{CaH}_2$ , a white crystalline substance which reacts with water, forming the hydroxide and hydrogen.

**Calcium Oxide.**—Calcium oxide, or lime, is a very important substance as everyone knows. It does not occur in nature, but is readily prepared by heating marble or limestone to a high temperature when the following reaction takes place,



This reaction is reversible and the conditions governing it will be considered in detail under calcium carbonate.

This process is carried out in furnaces called lime kilns. The more modern types of these kilns, Fig. 56, consist of a tall shaft of brick work with the interior somewhat egg-shaped in cross

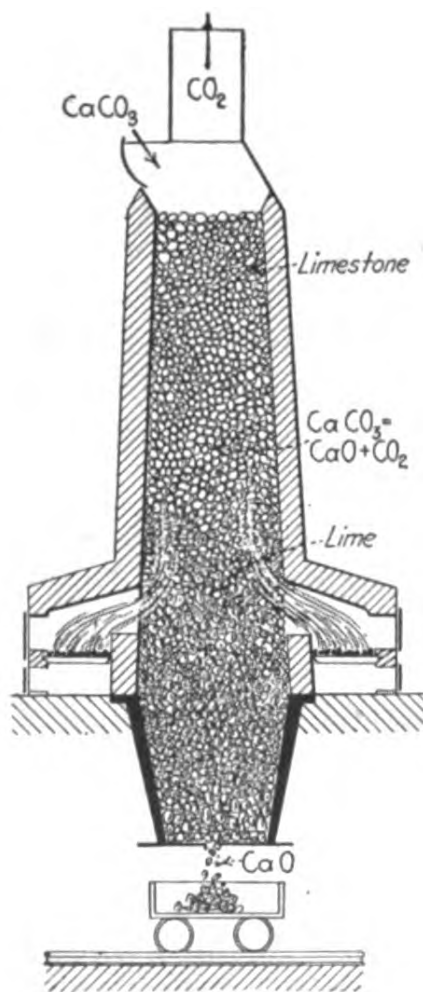


FIG. 56.

section, with two or more fire boxes located at the sides and opening into the shaft a short distance from the bottom. The flame and hot gases from the fuel are drawn into the shaft and heat the limestone above its temperature of decomposition, while the air drawn in by the draft of the stack sweeps away the carbon dioxide and so lowers the temperature necessary for the decomposition. The operation is continuous, the limestone being fed in at the top as fast as the lime is removed at the bottom. This country produces nearly four million tons of lime per year.

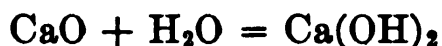
Calcium oxide is a white substance having a density of 3.3. It shows some signs of melting when heated in the oxyhydrogen blowpipe and under such conditions gives a very bright light which is known as the calcium or lime light.

The melting-point of lime is about  $1900^{\circ}$  and it not only melts easily at the temperature of the electric furnace, but even boils. When the vapors of the oxide condense, crystals of calcium oxide are formed. Calcium oxide is not reduced by sodium or by carbon except at temperatures of the electric furnace. The calcium obtained by the reduction with carbon unites with more carbon to form the carbide,  $\text{CaC}_2$ .

Lime has a great tendency to combine with water forming the hydroxide,  $\text{Ca}(\text{OH})_2$ . Because of this, it is used in drying ammonia and certain other gases and in dehydrating alcohol. Its

most important use, however, is in the preparation of mortar and cement.

**Calcium Hydroxide.**—Calcium hydroxide or slaked lime,  $\text{Ca(OH)}_2$ , is made by the action of water on calcium oxide or quicklime as it is sometimes called. The equation is,



The action is slow in starting but evolves considerable heat, so that after the reaction has once begun the temperature rises and it then goes on rapidly. When large quantities of lime slake in contact with wood, the temperature often rises high enough to set fire to the wood. In this way buildings containing lime in storage are sometimes set on fire by water in times of floods.

Calcium hydroxide is a white powder whose density is 2.08 and which therefore occupies a larger volume than the lime from which it was formed. It is slightly soluble in water, 600 parts of the latter being required for one of the hydroxide at ordinary temperatures, and about twice as much water at the boiling-point since the solubility of the hydroxide decreases with rising temperature. The solution is decidedly alkaline in character because calcium hydroxide is a strong base, although not as strong as sodium hydroxide. The solution of the hydroxide is called lime water and is used in medicine and as a reagent for the detection of carbon dioxide.

Because of its cheapness, calcium hydroxide is largely used wherever a base is desired, unless the properties of the calcium ion interfere. If the presence of much water is objectionable, a suspension of the hydroxide in water called milk of lime is used. That part which is actually in solution reacts first and then more dissolves so that ultimately it may all be used.

Slaked lime is used in the manufacture of sodium and potassium hydroxides, ammonia, bleaching powder, mortar, the softening of water, the purification of illuminating gas, the removal of hair from hides, and for many other purposes.

Air-slaked lime is lime which has been exposed to the air until it has fallen to powder from the water and carbon dioxide taken up from the air; it contains calcium oxide, hydroxide, and carbonate.

fore  $c$ , the concentration of the  $\text{CO}_2$  is constant for equilibrium at any one temperature. The concentration of a gaseous substance is proportional to its pressure, so it follows that the carbon dioxide in equilibrium with the  $\text{CaO}$  and  $\text{CaCO}_3$  at any given temperature will always have a certain fixed pressure.

The decomposition of the calcium carbonate is accompanied by the absorption of heat, and therefore in accordance with the law of mobile equilibrium the pressure of the carbon dioxide increases with rising temperature. It reaches atmospheric pressure at about  $900^\circ$ , but in a stream of air or any other gas which will keep the partial pressure of the carbon dioxide low by sweeping it away as fast as it is formed, the decomposition will take place at a much lower temperature. In the lime kiln the limestone is heated in a current of gases in which the partial pressure of carbon dioxide is far lower than one atmosphere, and consequently the temperature of decomposition is comparatively low.

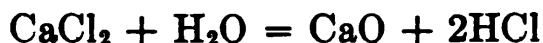
Calcium carbonate although so slightly soluble in water readily dissolves in acids. This of course is another case of a difficultly soluble salt of a weak acid being dissolved by a stronger acid.

**Calcium Chloride.**—Calcium chloride,  $\text{CaCl}_2$ , occurs in nature in sea water and as a constituent of a few minerals for example, tachhydrite,  $\text{CaCl}_2 \cdot \text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ , and apatite,  $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ .

It may be prepared by dissolving pure calcium carbonate in hydrochloric acid. It is a by-product of several technical processes and is comparatively cheap. It is exceedingly soluble in water and crystallizes with varying amounts of water of crystallization forming a mono, di, two tetrahydrates and hexahydrate. The hexahydrate crystallizes from highly concentrated solutions at ordinary temperatures. It is very deliquescent and melts at  $30^\circ$ . When mixed with ice in the best proportions, a temperature of  $-55^\circ$  may be obtained. Anhydrous  $\text{CaCl}_2$  and ice do not make a good freezing mixture since the salt evolves much heat in dissolving, while the hexahydrates absorb heat.

When the hexahydrate is heated to  $200^\circ$ , it loses four moles of water and forms a white porous mass of the dihydrate which is very hygroscopic and is used for drying gases. When heated to a still higher temperature the anhydrous salt is obtained but

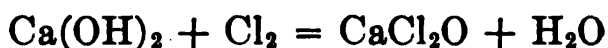
the reaction represented by the following equation takes place to a certain extent,



and the product contains some calcium oxide.

Calcium chloride forms a compound,  $\text{CaCl}_2 \cdot 8\text{NH}_3$ , with ammonia and cannot be used for drying this substance.

**Calcium Hypochlorite and Bleaching Powder.**—Bleaching powder,  $\text{CaCl}_2\text{O}$ , or chloride of lime, is made by the reaction of chlorine on slacked lime,



In the most recent plants, the slacked lime is carried in a conveyer in a direction contrary to that of the chlorine so that the almost saturated lime meets the strongest chlorine, while the fresh lime comes in contact with the weakest chlorine. In this way, each is utilized to the greatest advantage. (For the properties and use of bleaching powder see pp. 128, 133.)

Pure calcium hypochlorite,  $\text{Ca(OCl)}_2$ , may be prepared by neutralizing hypochlorous acid with calcium hydroxide. It finds no application.

**Calcium Bromide and Iodide.**—Calcium bromide and iodide are very similar to the chloride, but are even more soluble than the latter.

\* **Calcium Fluoride.**—Calcium fluoride,  $\text{CaF}_2$ , or fluorspar as it is commonly called, occurs in nature fairly abundantly. It crystallizes in cubes and is nearly insoluble in water. It melts at  $1,330^\circ$  and has to a marked degree the property of reducing the melting-point of the slags produced in metallurgical processes and has long been used for this purpose. When heated it becomes luminous at temperatures far below redness, and this gives rise to the term fluorescence.

Calcium fluoride is the source of other fluorine compounds, and is used in the preparation of hydrofluoric acid for etching glass and for other purposes.

**Calcium Nitrate.**—Calcium nitrate,  $\text{Ca(NO}_3)_2$ , is found in all fertile soils. It may be made by the action of nitric acid on the carbonate, and is manufactured on a large scale for use as a fertilizer at the plant for the manufacture of nitrogen com-

pounds from the air at Notodden, Norway. It is very soluble in water and forms a number of hydrates; that stable at ordinary temperatures is  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ . The anhydrous salt is used as a drying agent. When heated it gives calcium oxide, nitrogen peroxide, and oxygen.

**Calcium Sulfate.**—Calcium sulfate,  $\text{CaSO}_4$ , occurs in nature in two forms as anhydrite,  $\text{CaSO}_4$ , and as gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ; the latter is the more important since from it is made the valuable plaster of Paris and cement plaster.

Calcium and sulfate ions are present in sea water and gypsum is deposited soon after the concentration of such water begins. Without doubt this has been the origin of the great beds of gypsum which are found in various parts of the world. The United States has many such deposits, notably in New York, Michigan, Iowa, Ohio, Texas, Oklahoma, and Kansas. The total production of gypsum in the United States is about 2,500,000 tons per year, of which two-thirds is converted into plaster.

Besides the dihydrate or gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , calcium sulfate forms a hemihydrate,  $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$ , which is in equilibrium with the dihydrate and water vapor at  $107^\circ$  under a pressure of one atmosphere. When ground gypsum is heated from  $110$  to  $130^\circ$  its aqueous tension is greater than one atmosphere, and it rapidly decomposes, losing water and changing into the hemihydrate. The product obtained in this way is called plaster of Paris. When mixed with water to form a paste, it quickly hardens to a mass of interlaced crystals of the dihydrate. In so doing it increases materially in volume and fills perfectly a mould into which it may be poured; because of this it is much used in making plaster casts. By far the more extensive use for this product is as a plaster for the interior of buildings, and for such purposes the plaster of Paris sets too quickly. To overcome this, advantage is taken of the fact that many organic substances such as glue, sugar, glycerine, etc., will greatly increase the time of setting; such substances are called retarders and the plaster so treated is known as cement plaster. Cement plaster may also be made without retarder by using gypsum which is mixed with the proper amount of clay or dirt.

These plasters have many advantages over lime plasters for inside work and have very largely replaced them. One impor-

tant advantage is that they dry quicker and are much harder and stronger than the lime plasters. If plaster of Paris is mixed with a solution of common salt instead of pure water, its time of setting will be shortened.

Great care must be taken not to overheat the plaster or drive off all the water, since in these cases the plaster either will be too slow in setting or will not set at all. Such plaster is said to be "dead burned."

The solubility of gypsum varies in a rather remarkable way with the temperature; from 0° to 38°, the solubility increases and then decreases as the temperature rises. At the boiling-point of water, in a steam boiler working under the usual pressure, calcium sulfate is nearly insoluble; and under such conditions, it is precipitated from water which contains much of this substance, in the form of a scale which clings closely to the boiler. Hard boiler scale often consists largely of calcium sulfate. Waters containing this substance are said to have permanent hardness in distinction from temporary hardness due to the bicarbonate. The addition of the proper amount of sodium carbonate will precipitate the calcium as carbonate and leave a solution of sodium sulfate. In this way the permanent hardness may be removed.

**Calcium Sulfide.**—Calcium sulfide,  $\text{CaS}$ , is made by heating the sulfate with charcoal. It is a by-product of the Le Blanc soda process, and is insoluble in water; but is slowly hydrolyzed forming calcium hydroxide and the hydrosulfide,



Many specimens of calcium sulfide especially if slightly impure with compounds of vanadium and bismuth will phosphoresce, *i.e.*, shine in the dark, after being exposed to the light. The pure sulfide does not do this.

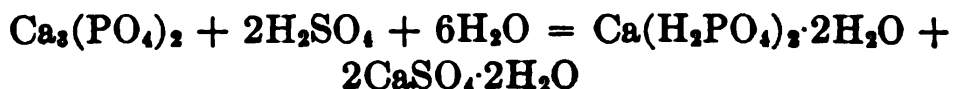
**Calcium Phosphate.**—The principal forms in which calcium phosphate occur in nature are apatite,  $\text{Ca}_5(\text{PO}_4)_3\text{F}$  and the normal phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ . Its chief commercial source is from phospherite whose composition lies between that of apatite and the normal salt. Enormous beds of phosphate are found in many parts of the world; notably in this country in Florida, Tenn-

essee, South Carolina, Utah and its neighboring States. The western deposit is the largest in the world and will doubtless at a future time furnish a large part of the supply.

Calcium phosphate is present in nearly all rocks and all fertile soils. It is practically insoluble in pure water, but is very slowly dissolved by the carbonic acid which is present in the ground waters. Compounds of phosphorus are absolutely essential to all forms of life. Animals derive what they need principally from plants, while the latter get theirs from the phosphate rendered soluble by the carbonic acid.

Although most soils contain in the aggregate large quantities of calcium phosphate, the action of the weather in rendering this soluble is too slow to meet the demands of the crops under intensive cultivation and hence the plants must be fed with ready prepared soluble phosphates. For this purpose many millions of tons of phosphorite are mined each year and made into "super-phosphate" fertilizer.

The phosphate fertilizers are made by mixing approximately equal quantities of phosphorite and chamber-sulfuric acid. The dihydrates of calcium sulfate and monocalcium phosphate are formed as shown in the following equation:

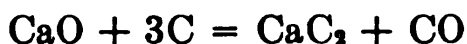


This reaction takes place with the evolution of heat, and the mixture soon solidifies to a mass composed of the two hydrated salts. This is known as superphosphate. The monocalcium phosphate is easily soluble in water, and is the more valuable part of the fertilizer.

Besides the tricalcium phosphate or normal phosphate as it is called,  $\text{Ca}_3(\text{PO}_4)_2$ , there is known the dicalcium salt,  $\text{CaHPO}_4$ , and the monosalt given above. All the calcium phosphates are readily soluble in acids, even in those as weak as acetic acid. This is due to the fact that phosphoric acid is weak and that ion,  $\text{H}_2\text{PO}_4^-$ , is formed with especial ease. The calcium salt of this ion is easily soluble as has been mentioned above.

Besides being made into fertilizers, calcium phosphate serves as the source of phosphoric acid and phosphorus.

**Calcium Carbide and Calcium Cyanamide.**—Calcium carbide,  $\text{CaC}_2$ , is formed by the reaction of carbon upon lime in an electric furnace (Fig. 57). The equation for the reaction is,



The carbide reacts with water producing acetylene, and with nitrogen for the formation of calcium cyanamide,  $\text{CaCN}_2$ ,

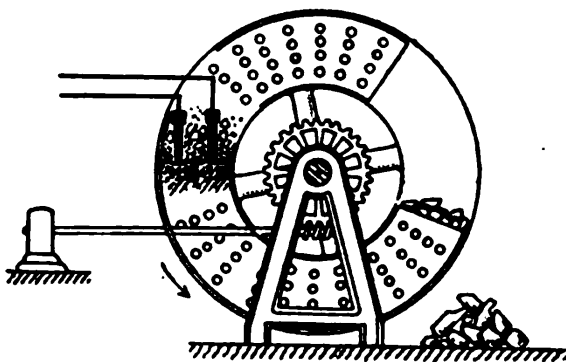


FIG. 57.

This reaction takes place at  $1,000^\circ$  and goes more readily in the presence of calcium chloride. Calcium cyanamide is slowly decomposed by water, forming the carbonate and ammonia,



It is therefore useful as a nitrogen fertilizer, and is now being made at Niagara Falls in the United States, and in about fourteen different places in the world. While the nitrogen fertilizers are very important, they are not as absolutely indispensable as the phosphates and potassium fertilizers are since it is practicable to introduce the nitrogen compounds into the soil with leguminous plants.

**Calcium Oxalate.**—Calcium oxalate,  $\text{CaC}_2\text{O}_4$ , is a white crystalline salt which is very slightly soluble in water and is formed at once whenever a solution of an oxalate is added to a calcium salt. The precipitate is practically insoluble in water and in acetic acid, but dissolves easily in strong acids like hydrochloric and nitric. The explanation for the difference is to be found in the fact that oxalic acid is a stronger acid than acetic, but weaker than hydrochloric. It will be recalled that the difficulty

soluble salts of weak acids are soluble in the stronger acids because of the decrease in the concentration of their anion due to the formation of the undissociated weak acid. The slight solubility of calcium oxalate is made use of in the detection and estimation of calcium as ion. The oxalate reagent used is ammonium oxalate.

**Calcium Silicate and Glass.**—Calcium silicate occurs in nature in almost all of the natural silicates. The meta silicate,  $\text{CaSiO}_3$ , forms the mineral wollastonite, but is not of much importance.

The artificial complex silicates known as glass are, however, of great importance. The most common of these, that known as soft or soda glass, is made from calcium carbonate, sodium carbonate, and glass sand, which is nearly pure silicon dioxide. The reaction may be represented by the following equation:

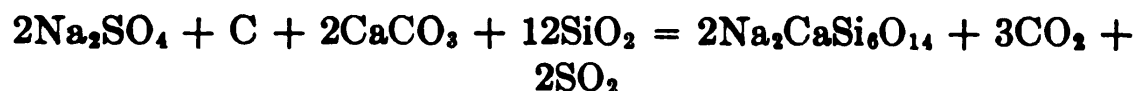


but it must be understood that the glass is a mixture of silicates rather than a definite chemical compound.

The substances are mixed in the proper proportions and heated to a temperature below their melting point when the reaction takes place, and most of the carbon dioxide escapes through the porous mass. The temperature is then raised to about  $1,200^\circ$  when the glass fuses to a mobile liquid which is fluid enough to allow the bubbles of gas to escape. The temperature is then lowered to  $700^\circ$  or  $800^\circ$  when the glass becomes viscous enough to work. Ordinary window glass is made by blowing long cylindrical bulbs of glass. After the bulb is blown to the proper dimensions the bottom is heated and blown out leaving a long cylinder with a bottle-like top and neck. This is allowed to cool and the top cut off by wrapping a string of hot glass around the cylinder near the top and suddenly touching a heated spot on the cylinder with a cold iron. A crack instantly extends around the cylinder following the line heated by the string of hot glass. The result is a long glass cylinder open at each end. This is then split lengthwise by running a red hot iron through the cylinder and touching the heated glass at the end with a cold iron. The crack instantly runs the whole length of the cylinder. This is then placed upon a flat revolving bed of a furnace upon which it is smoothed out after being heated to the softening point.

Bottles are blown into moulds, but flasks, beakers, etc., are made free hand without any moulds, the glass blower taking advantage of the fact that the surface tension of the glass will cause it to contract when heated, while he can make it expand at will by blowing into the vessel when it is hot. Glass tubing is made by rapidly drawing out a hollow mass of glass. This is done by two men who walk or run in opposite directions. Pressed glass articles are made by pressing the hot glass in moulds having the desired designs cut upon them. The designs in cut glass are worked into the glass with rapidly revolving wheels, armed with wet sand which quickly cuts away the glass. The surface is afterward polished. Plate glass is made by casting the glass into large sheets which are ground until the sides are plane and parallel, and then polished.

The cheaper kinds of soda glass are often made from sodium sulfate, carbon, calcium carbonate, and sand, the equation being,



Soda glasses are rather easily attacked by water, and for many chemical purposes the more difficultly soluble and less fusible potassium glass is made; this is practically the same as the soda glass except the potassium has taken the place of the sodium. Its composition may be represented by  $\text{K}_2\text{CaSi}_6\text{O}_{14}$ . It is commonly called hard or Bohemian glass. Curiously enough a glass composed of a mixture of soda and potash glass is more soluble than one containing either alone.

Many special glasses are made in which the sodium, potassium, and calcium are replaced more or less completely by lead, magnesium, zinc, barium, antimony, arsenic, aluminum, lithium, didymium, thallium, iron, manganese; and the silica by boric or phosphoric oxides. Flint glass, crystal glass, and Strass are potassium lead glasses and have great brilliancy and a high index of refraction. They are easily attacked by water and acids, and are not suitable for chemical purposes, but are used in optical instruments. One kind of Jena glass is especially resistive to chemical action and is a borosilicate glass containing zinc and barium.

Molten glass will dissolve many metallic oxides which often

impart characteristic colors. Cobalt gives blue, chromium and copper oxides green, uranium yellow with a greenish fluorescence, cuprous oxide with a reducing agent, selenium and metallic gold a deep red color due to a colloidal solution of the elements. Milk glass is made by adding bone ash (calcium phosphate) or stannic oxide,  $\text{SnO}_2$ , to the glass. These do not dissolve, but make the glass white and opaque.

Glass is an amorphous substance, and has no definite melting point; it simply gradually softens as the temperature is raised. This has led many to consider glass at ordinary temperatures as a very viscous liquid, but it certainly is highly elastic and has the general properties of a solid. When glass is kept for a long time at temperatures near its softening point, it gradually becomes crystalline or devitrifies as it is called. With certain kinds of glass, this seriously interferes with its working.

All thick glass objects, especially if of irregular shape, must be cooled very slowly, annealed as it is called. If cooled quickly, the outside will harden while the inside is still soft; upon further cooling, the interior tends to contract and this puts great stress upon the glass and makes it extremely likely to crack. A piece in this condition will often fly into minute fragments when scratched at any point on the surface.

**Analytical Properties of Calcium.**—The more important analytical properties of calcium have been given in connection with the oxalate. In addition it may be mentioned that volatile calcium compounds, the chloride for example, color the Bunsen flame brick red and give a red and a green band in the spectro-scope (see Frontispiece). The latter test is quite sensitive.

## STRONTIUM

Strontium is the second member of the alkaline earth metals, if they are arranged in the order of their atomic weights.

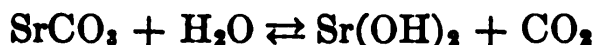
Both the physical and chemical properties of the element and of its compounds closely resemble those of calcium and the calcium salts. It is, however, much less abundant and is relatively unimportant.

The metal may be prepared by electrolysis of the fused chloride; it is silvery white and crystalline. It melts at  $800^\circ$

and volatilizes at  $950^{\circ}$  in a vacuum. The density is 2.5. It is more rapidly oxidized in air than calcium and decomposes water and alcohol. It dissolves very rapidly in acids. When heated in oxygen it burns with a bright red flame. It combines with most of the non-metallic elements. The atomic weight of strontium is 87.63.

**Occurrence.**—Strontium occurs in nature as strontianite, the carbonate,  $\text{SrCO}_3$ , isomorphous with aragonite and as celestite,  $\text{SrSO}_4$ , isomorphous with anhydrite,  $\text{CaSO}_4$ .

**The Compounds of Strontium.**—Besides the naturally occurring carbonate and sulfate, the principal compounds of strontium are the chloride,  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ , the nitrate  $\text{Sr}(\text{NO}_3)_2$ , the oxide,  $\text{SrO}$ , the hydroxide  $\text{Sr}(\text{OH})_2$ , and the oxalate  $\text{SrC}_2\text{O}_4$ . The salts may be easily made from the carbonate by treating the latter with the acid corresponding to the salt desired. The oxide may be made by a similar method to that used for calcium oxide, that is by heating the carbonate; but the temperature required is far higher than that for calcium oxide, so a better way is to heat strontium nitrate. The hydroxide may be easily made by passing superheated steam over the carbonate,



The steam sweeps away the  $\text{CO}_2$  as it is formed and so favors the transformation of the carbonate. Strontium chloride, sulfate and carbonate are less, while the hydroxide and oxalate are more soluble than the corresponding calcium compounds.

Volatile strontium compounds color the flame carmine red and give a spectrum which consists of a number of strong red lines and a weaker but more characteristic blue line. The spectroscopic test is very sensitive.

## BARIUM

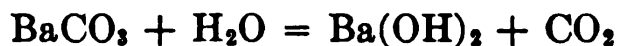
Barium is the third element of the alkaline earth family. The metal is silver white and has a density of 3.78. It melts at about  $850^{\circ}$  and boils at  $1,150^{\circ}$ . It oxidizes rapidly, sometimes catching fire spontaneously, and decomposes water and alcohol even more vigorously than strontium. It combines readily with hydrogen and nitrogen. The atomic weight of barium is 137.37.

**Occurrence.**—Barium occurs in nature principally as barytes or heavy spar which is barium sulfate,  $\text{BaSO}_4$ , and as the carbonate or witherite,  $\text{BaCO}_3$ . From these the other barium compounds are made. They are technically much more important than the corresponding strontium compounds. Barium salts may be obtained by treating witherite with the corresponding acid or by reducing the sulfate to sulfide with carbon at high temperatures, and treating the sulfide with the acid of the desired salt.

**Barium Oxide and Hydroxide.**—Barium oxide,  $\text{BaO}$ , is made by heating the nitrate to a high temperature. It is impracticable to prepare the oxide by heating the carbonate alone, since the temperature of decomposition is very high, but a mixture of carbon and barium carbonate reacts easily at a moderate temperature to form barium oxide and carbon monoxide,



The formation of the carbon monoxide aids by reducing the partial pressure of the carbon dioxide. The oxide combines even more readily with water than calcium oxide to form the hydroxide which is often called baryta,  $\text{Ba}(\text{OH})_2$ . Because of this, it is feasible to prepare the hydroxide by heating the carbonate in a stream of superheated steam,



The steam decreases the partial pressure of the carbon dioxide, and the opportunity for the formation of the very stable hydroxide aids in the reaction.

The hydroxide is more soluble in water than either the corresponding strontium or calcium compound and is a somewhat stronger base. It crystallizes from its solutions with 8 molecules of water,  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ .

**Barium Dioxide.**—Barium dioxide,  $\text{BaO}_2$ , is formed when either the oxide or hydroxide is heated in a stream of air. At a higher temperature, or lower pressure of oxygen, it decomposes into oxygen and barium oxide. This was the basis of a process for obtaining oxygen from the air. This process has now been replaced by that founded on the liquefaction of the air.

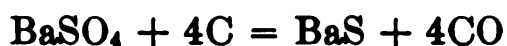
Barium dioxide is important as the starting point for the preparation of hydrogen dioxide.

**Barium Carbonate.**—Barium carbonate,  $\text{BaCO}_3$ , as has been mentioned, occurs in nature. It is also formed by bringing together a solution of a carbonate and a barium salt, or by fusing the sulfate with sodium carbonate. It is only slightly soluble, but more so than the carbonates of calcium or strontium. Its solubility in water is increased by the presence of carbon dioxide, owing to the formation of the bicarbonate.

**Barium Sulfate.**—Barium sulfate, barytes,  $\text{BaSO}_4$ , is in some respects the most important salt of barium. It is the chief source of the other compounds, and is itself extensively used as a white pigment, called "permanent white," which is used in paints. The precipitated barium sulfate is more valuable as a pigment than the natural because the particles are smaller and hence it has more "covering" power since it is not so transparent. This precipitated sulfate may be obtained by first dissolving witherite in hydrochloric acid, and then adding sulfuric acid which will precipitate the barium sulfate and regenerate the hydrochloric acid which is then ready to treat another lot of witherite. It may also be obtained by reducing the sulfate to sulfide,  $\text{BaS}$ , by carbon at high temperatures, and treating the extract from this, which will contain the hydroxide and the hydrosulfide, with sulfuric acid. The sulfate has some advantages over white lead as a pigment, in that it is chemically inert and cannot change in color, but it does not "cover" as well (see p. 422).

Barium sulfate is one of the least soluble salts; 100 gm. of water will dissolve 0.00026 gm. of the salt at  $25^\circ$ .

**Barium Sulfide.**—Barium sulfide,  $\text{BaS}$ , to which frequent reference has been made, is prepared by the interaction of carbon and the sulfate

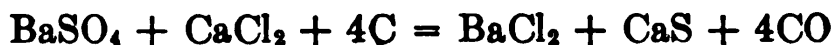


It is slowly attacked by water, forming the hydroxide and hydrosulfide.

Barium sulfide is phosphorescent when it contains certain impurities, although the pure compound is not.

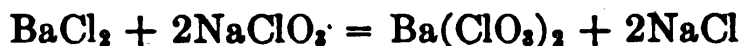
**Barium Chloride.**—Barium chloride,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ , is made by

heating a mixture of the sulfate with carbon, and calcium chloride,  $\text{CaCl}_2$ ,



The furnace product is treated with water to dissolve the barium chloride, which is purified by recrystallization. It is not as soluble as calcium chloride and is not deliquescent. It is much used as a reagent for the detection and determination of the sulfate ion. Like all the other soluble barium salts it is highly poisonous.

**Barium Chlorate.**—Barium chlorate,  $\text{Ba}(\text{ClO}_3)_2$ , is made by heating together, in solution, barium chloride and sodium chlorate



It is used in making green fire.

**Barium Nitrate.**—Barium nitrate,  $\text{Ba}(\text{NO}_3)_2$ , is made by the action of nitric acid upon the carbonate, sulfide, oxide or hydroxide of barium. It crystallizes as the anhydrous salt and sometimes is used in colored fire. It is used in the preparation of the oxide as noted above.

**Barium Chromate.**—Barium chromate,  $\text{BaCrO}_4$ , is precipitated by bringing together a barium salt in solution and a soluble chromate or dichromate. It has a yellow color and is one of the few colored barium salts. It is but slightly soluble in water and weak acids, but dissolves in strong acids. The chromates of calcium and strontium are very much more soluble than barium chromate; and advantage is taken of this in the analytical separation of the elements.

**Analytical Properties of Barium.**—The properties of barium which are used in analysis are the slight solubility of the carbonate, sulfate, and chromate together with the green color which it will impart to the Bunsen flame, and the spectrum which consists of a number of orange and green lines. These are much less intense than the lines of calcium and strontium so that this test is not very sensitive. In the separation of the group the members are precipitated together as the carbonates. The precipitate is then dissolved in acetic acid and potassium dichromate added which precipitates barium chromate. The solution is filtered

and a dilute solution, 5 grm. per liter, of potassium sulfate added. Since strontium sulfate is much less soluble than calcium sulfate, the concentration of the sulfate as ion in this dilute solution will precipitate strontium sulfate, but not that of calcium. The solution is then filtered and ammonium oxalate added to precipitate the calcium.

### RADIUM

The remaining member of the group is the very rare element, radium. This was discovered in 1898 by M. and Mme. Curie. It is widely distributed in nature, but always in very small quantities. All rocks and soils seem to contain a very little. It is most abundant in the minerals which contain uranium and there seems to be a more or less definite ratio between the radium and the uranium content of the ores.

The compounds of radium very closely resemble those of barium, and the corresponding compounds of the two elements are often isomorphous. Radium chloride, bromide, carbonate, and sulfate are less soluble than the corresponding barium salts. This decrease in solubility is in accord with its higher atomic weight, 226.0. The volatile compounds color the Bunsen flame carmine red and give two beautiful bands in the red, a line in the blue-green and two weak lines in the violet portion of the spectrum. The spectrum of radium is so distinct and characteristic that there can be no doubt but that it is an element. The radium compounds have the very remarkable property of being highly radioactive and of changing spontaneously into other elements, but the discussion of this phase of the subject will be postponed to a later point when the radioactive elements may be considered in a group.

Metallic radium has been obtained by first preparing the amalgam through the electrolysis of a solution of radium chloride using mercury as the cathode, and then carefully driving off the mercury by heating in a vacuum. The radium is left behind as a hard silvery white metal. It melts at  $700^{\circ}$  and is rather more volatile than barium. It blackens in the air, due to the formation of a nitride, acts upon water very vigorously. The radioactivity of the metal is the same as that of an equivalent quantity of one of its salts.

**General Relationships.**—As with the alkali metals, the properties of the alkaline earth elements vary in a regular way with the atomic weight as may be seen from the following table.

As the atomic weight increases.

The reactivity of the element increases.

The density of the element and compounds increases.

The basic properties of the hydroxide increase.

The solubility of the hydroxide increases.

The solubility of the halogen compounds and nitrate decreases.

The solubility of the sulfate and chromate decreases.

## CHAPTER XXIII

### THE MAGNESIUM SUB-GROUP

The members of this sub-group, beryllium, magnesium, zinc, cadmium, and mercury do not form as well marked a family as the members of the alkaline earth metals.

Beryllium is perhaps even more like the next group than it is like the other members of this and so makes a good connecting link between the two groups. Magnesium, zinc, and cadmium have many points in common but not as many as calcium, strontium and barium. Mercury differs markedly from the others as will be seen when its compounds are discussed. All the members of the sub-group are more readily reduced to the metallic state than are the members of the alkaline earths and are less active chemically.

#### BERYLLIUM OR GLUCINUM

The first member of the magnesium group is beryllium or glucinum as it is often called. It got the name glucinum from the fact that its salts have a sweet taste and the name beryllium from its occurrence in the gem stone beryl.

The element does not occur free in nature and its compounds are rare. Neither the element nor its compounds have found any application except that some of the latter are used as gems. Beryl, for example, is a double beryllium aluminum silicate,  $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ , which when transparent and green colored is known as emerald and when having a bluish-green tint as aquamarine. The color of emerald is probably due to chromium.

Metallic beryllium may be prepared by the electrolysis of the fused double fluorides of sodium or potassium,  $\text{BeF}_2 \cdot \text{NaF}$ . It is less active chemically than the metals of the alkaline earth group and decomposes water only very slowly, even when heated. It dissolves readily in the dilute acids, and in solutions of sodium or potassium hydroxides. Aluminum, the first metallic member

of the next group, shows this same peculiarity and this is but one of several indications that beryllium gives of its position as the connecting element between Groups II and III. It will be recalled that in discussing lithium it was pointed out that the first member of a group often had properties which connected that group with the next higher one.

The chloride,  $\text{BeCl}_2$ , and the sulfate,  $\text{BeSO}_4$ , are the best known salts. They are both soluble in water and their solutions react acid, owing to hydrolysis. The hydroxide,  $\text{Be}(\text{OH})_2$ , is very slightly soluble in water but dissolves in acids, and also in solutions of sodium or potassium hydroxide.

Beryllium carbonate is very unstable and decomposes in the air at temperatures below the boiling-point of water into the oxide and carbon dioxide.

The atomic weight of beryllium is 9.1.

## MAGNESIUM

Magnesium occurs very abundantly in nature as a component of a large number of silicates of which mention may be made of olivine,  $\text{Mg}_2\text{SiO}_4$ , serpentine,  $(\text{MgFe})_3\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ , asbestos,  $\text{Ca}_3\text{Mg}(\text{SiO}_3)_4$ , meerschaum,  $\text{H}_2\text{Mg}_3(\text{SiO}_3)_3 \cdot \text{H}_2\text{O}$ ; as the carbonate, magnesite,  $\text{MgCO}_3$ , and as a double salt with calcium carbonate,  $\text{MgCO}_3 \cdot \text{CaCO}_3$ , known as dolomite. The sulfates and chloride and mixtures of the double salts are found in Stassfurt. This by no means exhausts the list of its occurrence which might be greatly extended.

**Preparation of the Metal.**—Metallic magnesium is now prepared by the electrolysis of fused dehydrated carnallite,  $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ . The electrolysis is carried out in closed electric furnaces through which a current of hydrogen or coal gas is passed to protect the metal from the air.

Magnesium is a silver white metal having a density of 1.75. It melts at  $650^\circ$  and boils at  $1,120^\circ$ . When heated nearly to its melting-point it softens and may be pressed into wire which can then be rolled into ribbon. It preserves its luster in dry air but tarnishes in moist. When heated in the air it burns with a very intense light, forming a mixture of the oxide,  $\text{MgO}$ , and the nitride,  $\text{Mg}_3\text{N}_2$ . At a moderately high temperature, the

metal decomposes steam, forming hydrogen and the oxide. It will burn in carbon dioxide with the deposition of carbon and the formation of the oxide. As may be judged from these examples, magnesium is an excellent reducing agent.

The light produced when magnesium burns is especially rich in the violet rays which most affect the photographic plates and hence the metal finds application as the active component of "flash powder," which may be prepared from powdered magnesium and potassium chlorate or similar oxidizing agents. With aluminum, it forms useful alloys, which can easily be cast and worked and are lighter than aluminum.

The atomic weight of magnesium is 24.32.

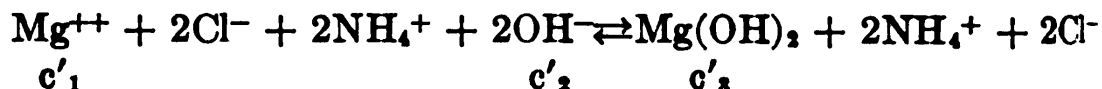
**Magnesium Oxide and Hydroxide.**—Magnesium oxide,  $\text{MgO}$ , or "calcined magnesia" is prepared by heating the carbonate, which breaks down into the oxide and carbon dioxide at a much lower temperature than calcium carbonate. It is a white, highly infusible substance, which is used as a lining for electric furnaces and for crucibles for use in the Goldschmidt process, p. 396. It slowly reacts with water to form the hydroxide,  $\text{Mg}(\text{OH})_2$ , which is only slightly soluble. The solution has a very faint alkaline reaction, due to the fact that the hydroxide is a weaker base than calcium, as well as being less soluble. Because of its slight solubility the hydroxide is precipitated when a soluble hydroxide is added to a magnesium salt. An exception to this is found in the fact that if ammonium salts are present in sufficient concentration, magnesium hydroxide is not precipitated by ammonium hydroxide. The explanation is as follows: Ammonium hydroxide is a weak base and the reaction represented by the equation,



takes place only to a slight extent with the formation of ammonium and hydroxyl ions. From the law of mass action,  $c_2 c_3 / c_1 = K$ . Ammonium salts are largely dissociated and give a high concentration of the ammonium ion. So, if some ammonium salt, say the chloride, be added to an ammonium hydroxide solution, the concentration of the ammonium ion,  $c_2$ , will be increased and this will cause a decrease in the concentration of the hydroxyl

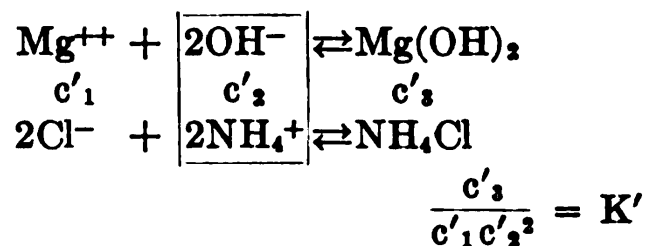
ion,  $c_3$ , and an increase in that of the undissociated hydroxide  $c_1$ . Ammonium hydroxide is then a weaker base in the presence of ammonium salts than when alone; and when the concentration of the salt is high, that of the hydroxyl ion becomes very small indeed.

When ammonium hydroxide is added to a magnesium salt, the reaction is represented by the following equation,



The conditions for equilibrium are represented by the equation  $c'_3/c'_1c'_2{}^2 = K$ . Now, before magnesium hydroxide can be precipitated, the solution must be saturated with the substance; which means the  $c'_3$  must have reached a certain definite value; and hence  $c'_1 c'_2{}^2$  must have attained a fixed and definite magnitude known as the solubility product or "precipitation value." When ammonium hydroxide is added to a magnesium salt in the *absence* of an ammonium salt,  $c'_3$  is large enough so that  $c'_1c'_2{}^2$  exceeds the solubility product of magnesium hydroxide and this compound is precipitated; but if an ammonium salt is present,  $c'_3$  will be so reduced as shown above that  $c'_1c'_2{}^2$  will be smaller than the solubility product, and  $\text{Mg}(\text{OH})_2$  will not be precipitated. Correspondingly, magnesium hydroxide is dissolved by ammonium salts, such as the chloride or nitrate.

This may be shown as follows:



The ammonium ion from the salt unites with the hydroxyl ions from the magnesium hydroxide, and thereby decreases  $c'_3$ ; this will, of course, decrease  $c'_3$ , and hence increase the solubility of the hydroxide.

Acids would, of course, act in much the same way and decrease the concentration of the hydroxyl ion through the formation of water. Their action, however, is more vigorous than that of ammonium salts. Many other hydroxides are affected in the

same way, so that the general rule may be formulated, that moderately soluble hydroxides will be dissolved by ammonium salts and even very difficultly soluble ones by acids, in each case, because of the decrease in the concentration of the hydroxyl ion.

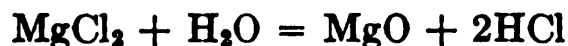
**Magnesium Carbonate.**—The normal carbonate occurs in nature as magnesite,  $\text{MgCO}_3$ . It also combines with calcium carbonate to form a compound called dolomite,  $\text{MgCO}_3, \text{CaCO}_3$ , which occurs in enormous quantities.

Magnesium carbonate is but slightly soluble in water, although more soluble than the hydroxide. It is more soluble in water containing carbon dioxide than in pure water, because of the formation of the bicarbonate.

When a soluble carbonate, such as sodium carbonate, is added to a magnesium salt, a mixture of magnesium carbonate and hydroxide is precipitated. The cause of the precipitation of the hydroxide is found in the fact that the sodium carbonate is hydrolyzed, giving a certain amount of the hydrocarbonate ion, and of the hydroxyl ion, in addition to the carbonate. Then, since magnesium hydroxide is even less soluble than the carbonate, the two salts are precipitated together.

This mixture prepared by precipitation is washed and dried and put on the market under the name of *magnesia alba*. It is used in medicine as a mild alkali.

**Magnesium Chloride.**—Magnesium chloride,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , is found in the Stassfurt salts and is called *bischofite*; it is very soluble and is highly deliquescent. When it is attempted to dehydrate the salt by heating, decomposition takes place and magnesium oxide and hydrochloric acid are formed as shown in the following equation:



Magnesium chloride forms a double salt with potassium chloride,  $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ , which is known as *carnallite*.

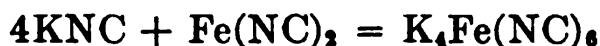
When *carnallite* is heated it loses its water of crystallization readily but the magnesium chloride is not decomposed. An ammonium magnesium double chloride,  $\text{MgCl}_2 \cdot \text{NH}_4\text{Cl} \cdot 6\text{H}_2\text{O}$ , isomorphous with *carnallite* is known. This may be dehydrated without decomposition of the magnesium chloride, and when

heated to a still higher temperature the ammonium chloride is driven off and anhydrous magnesium chloride is formed.

The term **double salt** has been used a number of times without definition. By it is meant a salt formed by the chemical union of two salts and characterized by the fact that its solution shows the properties of all the ions of the component salts.

A **complex salt** is similar to double salts in that it is formed by the chemical union of two or more salts, but differs in that its solutions do not exhibit the properties of the ions of the salts from which it was formed but instead some of these properties are found to have disappeared and to have been replaced by entirely new properties.

A typical complex salt is potassium ferrocyanide,  $K_4Fe(NC)_6$ . This may be formed by bringing together potassium cyanide, KNC, and ferrous cyanide,  $Fe(NC)_2$ ,



It might be expected to show the properties of potassium, ferrous, and cyanogen ions, but it shows the properties of potassium as ion and of a new very stable complex ion called ferrocyanogen,  $Fe(NC)_6^{--}$ , and not the properties of either ferrous or cyanogen ions. A salt of such a complex ion is called a complex salt. Complex salts and double salts gradually merge into one another, so that the difference is one of degree rather than kind.

**Magnesium Sulfate.**—Magnesium sulfate,  $MgSO_4$ , occurs in nature as kieserite,  $MgSO_4 \cdot H_2O$ , epsomite,  $MgSO_4 \cdot 7H_2O$ , schoenite,  $MgSO_4 \cdot K_2SO_4 \cdot 6H_2O$ , and in a number of other double salts in the Stassfurt deposits and in other places.

The hepta-hydrate or Epsom salts is an important compound, being used in the manufacture of potassium sulfate from the chloride, as a dressing for cotton goods, and in medicine as a purgative. It is freely soluble in water, and in this way differs strikingly from the sulfates of the alkaline earths and is like the sulfate of beryllium.

Schoenite,  $MgSO_4 \cdot K_2SO_4 \cdot 6H_2O$ , belongs to a rather large group of isomorphous salts which have the general formula,  $MAO_m \cdot m_2AO_4 \cdot 6H_2O$ , in which M stands for Mg, Zn, Cd, Ni, Fe, Mn, and m for K, Rb, Cs,  $NH_4$ , and A for S, Se, or Cr. These salts are

characterized by the fact that they readily lose their water of crystallization, in general, without the decomposition of the salt in other ways.

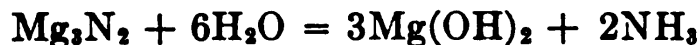
**Magnesium Sulfide.**—Magnesium sulfide,  $\text{MgS}$ , is made by the direct union of the elements. It is even more readily hydrolyzed than calcium sulfide, owing to the weakness of the hydroxide and its smaller solubility. By boiling the solution, all the sulfur may be obtained as hydrogen sulfide.

**Phosphates of Magnesium.**—Magnesium ammonium phosphate,  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ , is the most important phosphate of magnesium. Because of its slight solubility it is formed whenever magnesium, ammonium, and phosphate ions are brought together. The solution must be alkaline in order to have a sufficient amount of the phosphate ion  $\text{PO}_4^{--}$  present (see sodium phosphate, p. 290), and hence the solution must contain ammonium salts to prevent the precipitation of  $\text{Mg}(\text{OH})_2$ . The precipitate is of course soluble in acids, since phosphoric acid is weak. This compound is analytically the most important of the magnesium salts, since magnesium is always detected and determined through its formation. When magnesium ammonium phosphate is heated, it decomposes into magnesium pyrophosphate,  $\text{Mg}_2\text{P}_2\text{O}_7$ , ammonia and water,



In quantitative analysis, magnesium is weighed as the pyrophosphate.

**Magnesium Nitride.**—Magnesium nitride,  $\text{Mg}_3\text{N}_2$ , is formed by the interaction of magnesium and nitrogen at a fairly high temperature. It reacts with water to form ammonia and magnesium hydroxide,



**Analytical Reactions of Magnesium.**—Compounds of magnesium do not color the Bunsen flame, and consequently no spectrum is to be obtained in this way; but by passing electric sparks between pieces of the metal, a characteristic spectrum may be secured. The analytical importance of the magnesium ammonium phosphate has been discussed. The ion and all

of its compounds which do not contain colored anions are colorless.

**Water Softening.**—Natural waters almost invariably contain bicarbonates, chlorides, sulfates, and occasionally nitrates of calcium, magnesium, sodium, potassium, iron, and aluminum and also some free carbonic acid and silica. Of course, they sometimes contain other salts and acids in addition. For example, free sulfuric acid is often found in mine waters and in river water in the vicinity of factories using this acid.

Waters which contain calcium and magnesium salts are called hard waters and are a source of considerable annoyance and expense in the household, owing to the fact that calcium and magnesium soaps are practically insoluble, and that before a lather can be produced, soap must be added equivalent to all such salts which are present. The calcium and magnesium soaps so produced form a dirty disagreeable scum and are objectionable from every point of view. Many of the calcium and magnesium salts also cause a great deal of trouble and expense through the formation of "scale" in steam boilers, which not only increases the cost of repairs, but also causes a great waste of fuel. Magnesium salts are somewhat hydrolyzed, owing to the weakness of magnesium hydroxide and hence are acid in reaction. This is often the cause of serious pitting of boilers.

It is very desirable, therefore, that the salts of calcium and magnesium be removed from the waters before they are used for domestic or boiler purposes. This may be readily done at a cost far less than that of the soap, repairs and extra fuel, which would otherwise be required. For the removal of the objectionable salts, advantage is taken of the fact that calcium carbonate and magnesium hydroxide are nearly insoluble in water, and the treatment is so managed that these salts shall be precipitated. This is done by adding the proper amount of slaked lime and of crude sodium carbonate, or soda ash as it is called, to the water. The quantities to be added are calculated from the analysis of the mineral content of the water. Before treatment, the average water will contain free carbonic acid, bicarbonates, sulfates, and chlorides of magnesium, calcium, and sodium or more correctly, it will contain the corresponding ions. After treatment it will contain sulfate and chloride of sodium

and the slight amount of calcium carbonate and magnesium hydroxide corresponding to the solubilities of these compounds, which is so small that it may be neglected.

Enough sodium carbonate is added so that the total of the sodium ion originally present plus that added shall equal in equivalents the sulfate and chlorine ion present in the untreated water. Calcium hydroxide is added in sufficient amount to neutralize any free acid, to change all the hydrocarbonate ions to carbonate and to precipitate the magnesium as hydroxide.

What promises to become an important method for softening water is based upon the fact that when a hard water is filtered slowly through a bed of artificial zeolite,  $\text{NaAlSiO}_4 \cdot 3\text{H}_2\text{O}$ , called "permutite" the calcium, magnesium, manganese, and iron are automatically removed and replaced by sodium from the zeolite. The filtering medium becomes exhausted, but may be rejuvenated by treatment with a strong solution of sodium chloride which reverses the action and dissolves the calcium, magnesium, etc., replacing them by sodium.

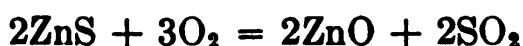
## ZINC

**General.**—Starting with beryllium, zinc is the third member of the magnesium sub-group. It does not occur as abundantly in nature as magnesium, but is of far more importance technically. The world's annual production of metallic zinc is about 880,000 tons, of which the United States furnishes about 30 per cent. Kansas, Missouri, Wisconsin and New Jersey are the chief zinc producing states.

**Occurrence.**—The principal ores of zinc are the sulfide,  $\text{ZnS}$ , known as sphalerite, blende, rosin-jack, or black-jack; the carbonate,  $\text{ZnCO}_3$ , called smithsonite, zinc spar and sometimes, though improperly, calamine; the silicates, calamine,  $\text{Zn}_2\text{H}_2\text{SiO}_6$  and willimite,  $\text{Zn}_2\text{SiO}_4$ ; and franklinite,  $(\text{FeZnMn})(\text{FeO}_2)_2$ .

**Metallurgy.**—The ores are first concentrated by crushing and washing away the lighter rock materials with water or in the case of the sulfide, by the recently devised flotation process which is rapidly increasing in popularity. In the latter process the ore is finely crushed and thoroughly churned up with air, oil and water. The ore particles, oil globules, and bubbles of air unite

to form an aggregate which is lighter than water and so floats off as froth while the worthless rock sinks to the bottom. The ores which contain the silicates or oxides of zinc merely require drying to remove the water before they are ready for reduction, but the carbonate should and the sulfide must be converted into the oxide before further treatment. The carbonate changes to the oxide when heated to a very moderate temperature, being like magnesium carbonate in this respect. The sulfide must be roasted in the presence of air when the oxide and sulfur dioxide are formed:



A part of the sulfur dioxide so produced is used to make sulfuric acid, and now furnishes about 250,000 tons of this substance per year.

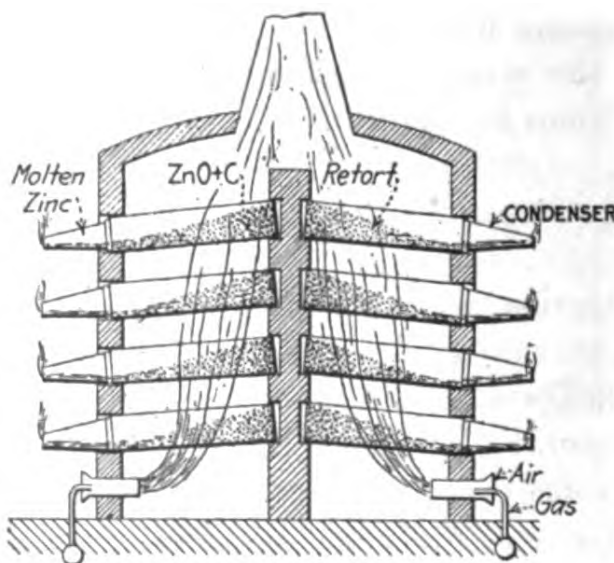
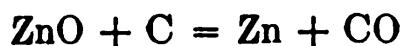


FIG. 58.

After getting the zinc in the form of anhydrous silicate or oxide, the next step is to reduce with carbon in a fire-clay retort furnace, Fig. 58. The equation for the chief reaction is



The temperature of reduction is about  $1200^\circ$ , while the boiling-point of zinc is  $906^\circ$ ; hence, the zinc will be vaporized as rapidly as formed, and provision must be made to catch and condense the vapors.

When the condenser is cold, that is below  $419^\circ$ , the melting-

point of zinc, the metal collects in the form of a fine powder which contains a few per cent. of the oxide, and is known as zinc dust; when it is above  $419^{\circ}$ , the zinc collects in the liquid state and is tapped off and cast into moulds forming what is known as spelter.

Under the best working conditions, the loss is great, as indicated by the bluish-green color of the flames burning at the mouths of the condensers, and the great amount of zinc oxide fumes which are given off and lost. An electrolytic process has recently been developed to the commercial stage in this country. The ore is roasted at a low temperature which produces  $\text{ZnO}$  and  $\text{ZnSO}_4$ . The product is extracted with dilute sulfuric acid, and the resulting impure solution of zinc sulfate is purified and then electrolyzed, the zinc being deposited at the cathode. It is more than 99.99 per cent. pure and commands a premium on account of its purity.

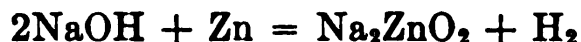
**Physical Properties.**—A fresh surface of pure zinc is brilliantly white, but quickly tarnishes and then has the familiar bluish-gray tinge. It melts at  $419^{\circ}$  and boils at  $906^{\circ}$ . Cast zinc is crystalline and very brittle, but when heated to between  $100^{\circ}$  and  $150^{\circ}$ , it becomes malleable and may be rolled into thin sheets or drawn into wire. At about  $200^{\circ}$  it again becomes brittle and may be powdered in a mortar. The density of the cast zinc is about 6.93 and of the rolled 7.18.

**Chemical Properties.**—Zinc belongs to the more active of the elements, but is far less so than the alkali or alkaline earth metals. It is not affected by dry air at ordinary temperatures, but burns brilliantly above  $500^{\circ}$ . In ordinary air which contains water vapor and carbon dioxide, it quickly becomes covered with a basic carbonate which acts as a protective coating and keeps the rest of the metal from further corrosion.

The behavior of zinc toward dilute sulfuric acid is very peculiar in that while the commercial metal dissolves easily, very pure zinc is not attacked until it is touched by a piece of copper, platinum, carbon, etc., then the evolution of hydrogen begins, but on the copper, etc., and not on the zinc. However, the zinc passes into solution while the copper is unchanged. The explanation is found in the fact that it is very difficult for hydrogen as ion to change to hydrogen gas at the surface of zinc; so much so that the action is prevented with the pure metal. But if copper

is in contact with the zinc, the change of hydrogen as ion to hydrogen gas takes place easily on the copper, and the positive charges of the hydrogen ion are conducted from the copper to the zinc and change the latter into the zinc ion.

Sodium or potassium hydroxide will slowly dissolve zinc forming hydrogen and zincate:



Zinc is used in making brass, which is 63 to 70 per cent. copper and 37 to 30 per cent. zinc; in many other alloys; in electric batteries; and especially in galvanizing iron.

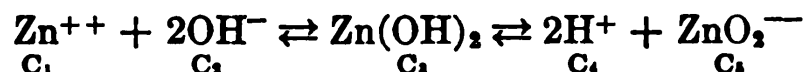
**Galvanized Iron.**—Two-thirds of the zinc produced per year goes into galvanized iron, that is, iron coated with a layer of zinc. This resists the action of the weather better than plain iron, because the zinc oxidizes first and so protects the iron. The iron is coated with zinc in three ways: first, by dipping very clean sheets of iron into molten zinc; second, by electrically depositing zinc upon cathodes of iron from properly prepared solutions of zinc salts; third, by the process known as sherardizing, which consists in exposing the cleaned iron object to the vapors of metallic zinc. In some ways this last method has the advantage, because the zinc and iron adhere better than they do by the other methods.

**Zinc Oxide and Hydroxide.**—Zinc oxide,  $\text{ZnO}$ , or zinc white, is by far the most important manufactured compound of zinc, and is prepared on a very large scale, 59,000 tons per year, either directly from the ores or from the metal. In this country the ores are used exclusively and the process is briefly as follows: the ore, either franklinite or roasted sulfide, is mixed with anthracite coal and charged into a furnace upon a brisk fire of hard coal with a good draft of air; the zinc oxide is reduced, the metal volatilizes, and then is reoxidized, forming a very fine white powder which is carried along with the flue gases until well cooled, and is then collected in cloth bags which act as filters. The product is used as a pigment in paints, in rubber goods, as a starting point for the manufacture of other zinc compounds, and as a base for ointment in medicine. Its largest single use is in paints. It is not as poisonous as white lead, and does not blacken with hydrogen sulfide. A paint containing zinc oxide as the

only pigment gets very hard and brittle, so it is unsuited for exterior work; but a mixture of white lead (basic lead carbonate) and zinc white is a great favorite and lasts better than either alone. Rubber goods consume a great deal of zinc oxide, automobile tires alone are said to require 40,000,000 lb. a year.

Zinc oxide is yellow when hot and white when cold. The change is due to a shift in the region of the absorption of light from the invisible to the visible part of the spectrum.

The hydroxide is not formed by the combination of the oxide and water, but may be obtained by adding a soluble base to a zinc salt. It is a white difficultly soluble substance which dissolves either in acids or in an excess of sodium or potassium hydroxide. This is due to the fact that zinc hydroxide not only yields zinc and hydroxyl as ion, but also dissociates to give hydrogen and zincate,  $\text{ZnO}_2^{--}$ , ions:

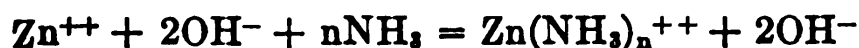


This action is typical of a number of hydroxides and hence calls for a rather full explanation. We have in these cases simultaneous and dependent equilibria between the hydroxide and the two sets of ions. The mass law equations in this case are

$$\frac{c^3}{c_1 c_2^2} = K \text{ and } \frac{c_4^2 c_5}{c_3} = K'$$

If an acid is added, its hydrogen ion will combine with the hydroxyl and thus reduce  $c_2$  and hence decrease  $c_3$  making the solution unsaturated and causing  $\text{Zn}(\text{OH})_2$  to dissolve and increasing  $c$ . If on the other hand, a strong base is added the hydroxyl from the base will combine with the hydrogen ion from the zinc hydroxide and hence reduce  $c_4$  thus causing  $c_3$  to decrease and the precipitate to dissolve to form a solution containing zincate ion,  $\text{ZnO}_2^{--}$ .

Zinc hydroxide is also soluble in excess of ammonia, due to the formation of a complex zinc ammonia ion,

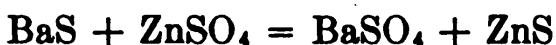


**Zinc Chloride.**—Zinc chloride,  $\text{ZnCl}_2$ , may be made by the combination of the elements; by the action of hydrochloric acid on zinc, or on the oxide or the carbonate. It is a white, very

deliquescent substance, which has a caustic action on the tissues. When a concentrated solution of the salt is mixed with zinc oxide, the whole sets to a hard mass of the oxychloride,  $\text{Zn}(\text{OH})\text{Cl}$ , hence the mixture is used as a cement. Solutions of the chloride have been successfully employed in the treatment of wood to prevent decay and in other cases as an antiseptic and a deodorant.

Zinc chloride either in solution or in the fused state has the power of dissolving the oxides of the metals; so it is used as a flux in soft soldering to clean the surfaces to be joined by the solder.

**Zinc Sulfate.**—Zinc sulfate,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , occurs in a hydrated form in nature to a small extent. It is known commercially as zinc vitriol or white vitriol. It may be prepared by the action of sulfuric acid on zinc oxide or metallic zinc or by very careful roasting of  $\text{ZnS}$ . It is a colorless salt, very soluble in water. It finds considerable use in medicine, in dyeing, in the manufacture of glue, and in the preparation of a zinc sulfide and barium sulfate mixture known as lithophone which has been used as a white pigment, but is not durable.



**Zinc Carbonate.**—Zinc carbonate,  $\text{ZnCO}_3$ , occurs in nature as smithsonite and is of considerable importance as an ore of zinc. A basic carbonate is precipitated upon the addition of a soluble carbonate to a solution of a zinc salt. The term basic salt is applied to a mixed salt containing hydroxyl or oxygen and some other anion; frequently the basic salts are mixtures of the hydroxide or oxide with the other salt, but very often they are true chemical compounds.

**Zinc Sulfide.**—The occurrence of zinc sulfide,  $\text{ZnS}$ , in nature has already been discussed. It is commonly known as blende and in its pure state is nearly white, but it shades to brown and even black depending upon the impurities it contains. It may be precipitated by the addition of ammonium sulfide or hydrogen sulfide to solutions of zinc salts. In this form, it is a fine white amorphous powder and is used as a pigment. Of the ordinary heavy metals, zinc is the only one that forms a white sulfide. It is soluble in dilute acids, and hence must be precipitated from neutral solutions. If the precipitation is to be complete, the

concentration of the hydrogen ion must be kept low. This may be done by adding an acetate to the solution. Most of the hydrogen is withdrawn in this way from the solution to form undissociated acetic acid. Zinc sulfide is infusible and very difficultly volatile. Its most important use is in the extraction of the metal.

**Analytical Properties of Zinc.**—Analytically, zinc is in a group with manganese, nickel and cobalt. These all have the common property of being precipitated as their sulfides by ammonium sulfide, but not by hydrogen sulfide in acid solution. Zinc and manganese sulfides are soluble in dilute sulfuric acid, while cobalt and nickel sulfide are practically unaffected. Zinc is distinguished from manganese by the fact that its hydroxide is soluble in an excess of potassium hydroxide, while that of manganese is not. From this alkaline solution, hydrogen sulfide will reprecipitate white zinc sulfide. The color of the sulfide is very characteristic, for it is the only common sulfide of a heavy metal which is white. The facts that the oxide is yellow when hot and white when cold, and that a green mass is formed when the oxide is wet with cobalt nitrate solution and then strongly heated are used in analytical work.

### CADMIUM

Cadmium is an element which is very closely allied to zinc in its properties and is found in nature in comparatively small amounts associated with this metal. The boiling-point of cadmium is much lower than that of zinc, consequently it is present quite largely in the first portions of the distillate obtained in the preparation of the latter metal. It may be freed from the zinc by repeated distillations at as low a temperature as possible, in an atmosphere of hydrogen to prevent its oxidation. This product may be further purified by electrolysis, a solution of  $\text{CdSO}_4$  being used as the electrolyte.

The element thus obtained is a bluish-white soft metal of a crystalline structure, density 8.64, melting at  $321^\circ$  and boiling at  $766^\circ$ . The molecular weight as determined from the vapor density is very nearly 112.4, the number which represents the atomic weight, consequently the formula is  $\text{Cd}$ .

and in the extraction of gold and silver from their ores, since it readily forms amalgams with these metals. Amalgams, as the alloys of mercury are called, are formed by nearly all of the metals. Iron and platinum are generally exceptions, but even these may be amalgamated under special conditions.

Pure mercury does not wet glass but runs around on it in clean round drops. When it contains even a small quantity of foreign metal it becomes covered with a film of oxide and then when it runs on glass, it strings out or forms a tail. This is a fairly sensitive test for impurities in the mercury.

It is interesting to note that mercury is the only metal which is liquid at ordinary temperatures, although cesium melts at temperatures which are often reached during the summer.

**Chemical Properties.**—Mercury does not oxidize upon exposure to the air at ordinary temperatures, but does so very slowly at about  $300^{\circ}$ , forming mercuric oxide. This fact was of great importance in the development of the present conception of combustion. (See p. 16.)

Mercury combines readily with sulfur and the halogens. It is not attacked by dilute hydrochloric or sulfuric acids, since the hydrogen as ion from these is not a strong enough oxidizing agent to oxidize the mercury to ion. It is dissolved by nitric acid or by hot sulfuric acid with the reduction of a part of the acids, and the evolution of nitric oxide or sulfur dioxide instead of hydrogen.

The compounds of mercury which are soluble enough to be absorbed by the human system are decidedly poisonous, but mercury in large drops is not. If, however, the mercury is very finely divided as it is in "blue mass" or in the form of vapor it exhibits its poisonous action. Mercury compounds are extremely poisonous toward bacteria and enough of the metal dissolves in pure water to kill these organisms in a short time. Mercury forms two series of compounds. In the one, it is divalent; and in the other it is at least apparently monovalent. The monovalent compounds are called mercurous and the divalent mercuric salts, and it is through the latter that the element establishes its connection with the magnesium group. The mercurous compounds will be discussed first.

## MERCUROUS COMPOUNDS

**Mercurous Oxide.**—Mercurous oxide,  $\text{Hg}_2\text{O}$ , is a blackish-brown substance which is formed by the action of an excess of lithium or potassium hydroxide upon a mercurous salt. It is not soluble in water and is very unstable, breaking down under the action of light or moderately high temperature into mercury and mercuric oxide. Mercurous hydroxide is unknown.

**Mercurous Chloride.**—Mercurous chloride or calomel,  $\text{HgCl}$  or  $\text{Hg}_2\text{Cl}_2$ , is the most important mercurous salt. It is very difficultly soluble in water and may be precipitated by adding a solution containing chlorine ions to a solution of mercurous nitrate. It is usually prepared by subliming a mixture of mercuric chloride,  $\text{HgCl}_2$ , and mercury,

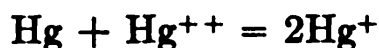


Mercurous chloride or calomel is largely used in medicine because it stimulates the liver and other organs producing the secretions. The vapor pressure of mercurous chloride reaches the atmosphere below the melting-point, and therefore the substance sublimes. Unless very pure, it should be protected from light which decomposes the ordinary salt, forming mercury and mercuric chloride which is very poisonous.

**Mercurous Bromide.**—Mercurous bromide,  $\text{HgBr}$ , is precipitated, as a white powder, by adding a bromide to mercurous nitrate.

**Mercurous Iodide.**—Mercurous iodide,  $\text{HgI}$ , may be formed directly from the elements or by precipitation from mercurous nitrate by an iodide. It is unstable and changes into mercury and mercuric iodide. The change takes place easily in the presence of an excess of  $\text{KI}$ , since the latter dissolves the mercuric iodide formed.

**Mercurous Nitrate.**—Mercurous nitrate,  $\text{HgNO}_3 \cdot \text{H}_2\text{O}$ , is the most important soluble mercurous salt. It is made by acting upon an excess of mercury with cold dilute nitric acid. It hydrolyzes, forming a basic nitrate,  $\text{Hg}_2(\text{OH})\text{NO}_3$ , which is but slightly soluble. Hence, a clear solution of the salt must contain nitric acid. Some metallic mercury should be kept in the solution to reduce any mercuric ion which might form,

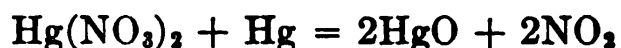


**Mercurous Sulfate.**—Mercurous sulfate,  $\text{Hg}_2\text{SO}_4$ , may be prepared by the action of hot-concentrated sulfuric acid upon an excess of mercury, or by adding the dilute acid to a mercurous nitrate solution. It may also be obtained by the electrolysis of dilute sulfuric acid using mercury as anode. It is white and but slightly soluble in water, but more so than the chloride. It is used in the construction of standard cells for the comparison of electromotive forces.

**Mercurous Sulfide.**—Mercurous sulfide,  $\text{Hg}_2\text{S}$ , is very unstable and can exist only at temperatures below  $-10^\circ$ ; at ordinary temperatures it decomposes into mercuric sulfide and mercury.

### MERCURIC COMPOUNDS

**Mercuric Oxide.**—Mercuric oxide or red precipitate,  $\text{HgO}$ , is usually prepared by heating an intimate mixture of mercuric nitrate and mercury until no more red fumes of nitrogen peroxide are given off.



When a solution of potassium or sodium hydroxide is added to a mercuric salt, a yellow precipitate of very finely divided mercuric oxide is formed. This precipitate is more active chemically and therapeutically than the coarser red oxide.

When mercuric oxide is heated it darkens, becoming almost black, and at a red heat it is decomposed into the elements. It will be recalled, it was through this reaction that Priestly discovered oxygen. Mercuric oxide is very poisonous, but is used in medicine.

Mercuric hydroxide is so unstable that it has not yet been prepared. The mercuric salts of the oxy-acids are highly hydrolyzed, so it must be a very weak base.

**Mercuric Chloride.**—Mercuric chloride or corrosive sublimate,  $\text{HgCl}_2$ , may be made by the direct combination of the elements at a slightly elevated temperature. The combination takes place with a peculiar green flame.

The salt is usually obtained as a crystalline sublimate by heating a mixture of mercuric sulfate, common salt, and a little

manganese dioxide, the latter being added to oxidize any mercurous sulfate which may be present.

It is much more soluble in hot water than in cold. It is soluble in alcohol and ether and a number of other organic solvents. An aqueous solution is slightly acid, indicating some hydrolysis, but no basic salt is deposited as is the case with mercuric nitrate and sulfate. The explanation for this is furnished in the fact that as indicated by the electrical conductivity, the halogen compounds of mercury are but slightly ionized, while the sulfate and nitrate and the salts of other oxyacids are strongly dissociated. The inevitable results of this would be that the mercuric salts of the oxyacids would hydrolyze further than the halides. In this connection it will be recalled that the halogen compounds of cadmium were less dissociated than the salts of the oxyacids.

Mercury compounds are highly poisonous to all forms of life, and mercuric chloride is much used as an antiseptic. For this purpose it is often put up in tablets with sodium chloride which makes it dissolve more rapidly. It is used in medicine both internally and externally, but because of its highly poisonous nature must be used very cautiously. Its antidote is white of egg, with which it forms a difficultly soluble compound. This should be removed by a stomach pump and magnesium sulfide administered to precipitate the last traces of mercury.

**Mercuric Bromide and Iodide.**—Mercuric bromide,  $\text{HgBr}_2$ , is much like the chloride, but is less soluble in water; it is also less dissociated than the chloride. Mercuric iodide,  $\text{HgI}_2$ , is but slightly soluble in water and is formed as a yellow precipitate which rapidly becomes scarlet when a solution of an iodide is added to a solution of a mercuric salt. It dissolves freely in solution of potassium iodide forming a colorless very soluble complex salt,  $\text{K}_2\text{HgI}_4$ , which fails to give most of the reactions of mercury; for example, potassium hydroxide does not precipitate mercuric oxide. After the addition of potassium hydroxide, the solution is called Nessler reagent, and is very sensitive toward ammonia which gives a yellow precipitate having the formula  $\text{Hg}_2\text{NI} \cdot \text{H}_2\text{O}$ .

Mercuric iodide exists in the two forms; the scarlet, stable from ordinary temperatures to  $126^\circ$ , and the yellow, stable above this temperature up to the melting-point,  $253^\circ$ .

Mercuric iodide and its complex potassium salt are used in medicine.

**Mercuric Nitrate.**—Mercuric nitrate,  $\text{Hg}(\text{NO}_3)_2$ , is prepared by dissolving the metal in hot nitric acid, and boiling until a portion of the solution does not yield a precipitate of mercurous chloride upon the addition of a chloride. It forms colorless very deliquescent crystals having the composition  $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ , easily soluble in water. It is easily hydrolyzed, precipitating a yellow basic salt.

**Mercuric Sulfate.**—When mercury is heated with concentrated sulfuric acid, mercuric sulfate,  $\text{HgSO}_4$ , water, and sulfur dioxide are formed. The mercuric sulfate so obtained is a white crystalline salt which is easily soluble in water containing sulfuric acid but hydrolyzes in pure water forming a yellow basic salt  $\text{Hg}_3(\text{SO}_4)_2\text{O}_2$ .

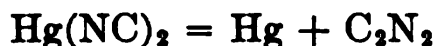
**Mercuric Sulfide.**—The most stable compound of mercury is the sulfide,  $\text{HgS}$ . This exists in the two forms, black amorphous and red crystalline. The latter occurs in nature as cinnabar and is the most important ore of mercury. As is the general rule, the amorphous form is the less stable and the more soluble of the two, but both are exceedingly slightly soluble substances. The black form is precipitated whenever hydrogen sulfide or a soluble sulfide acts upon a mercuric salt. It is somewhat soluble in sodium and potassium sulfide forming in the case of the sodium sulfide a white crystalline salt,  $\text{Na}_2\text{HgS}_2 \cdot 8\text{H}_2\text{O}$ . From this solution the less soluble red crystalline form is gradually deposited. The red crystalline modification may also be obtained by subliming the black. The artificial red sulfide is called vermilion and is used as a pigment.

Both forms of mercuric sulfide are very stable and are not attacked by hydrochloric acid or by dilute nitric acid hot or cold. The compound is dissolved by aqua regia, the sulfur being liberated as free sulfur or oxidized to the sulfate. Mercuric sulfide is the most stable sulfide of the metals and this is utilized in the analytical separation and identification of the metal.

**Mercuric Cyanide.**—Mercuric cyanide,  $\text{Hg}(\text{NC})_2$ , resembles the halogen compounds of mercury in many ways. It is more

soluble than the halides, but is even less dissociated than these, and its solution is a very poor conductor of electricity.

When heated, mercuric cyanide decomposes into mercury and cyanogen,  $C_2N_2$ ,



and this furnishes a very convenient method for the preparation of cyanogen.

**Mercury Fulminate.**—When mercury is dissolved in hot nitric acid and alcohol added to the still hot solution, a white precipitate of mercury fulminate,  $Hg(ONC)_2$ , is soon formed. This, when dry, explodes upon being struck, and is used in percussion caps and in the caps for exploding guncotton and dynamite.

**Complex Compounds of Mercury.**—Mercury forms a very large number of complex compounds far too large for them all to be considered in detail or even mentioned in a book of this kind. The nitrogen compounds, however, demand a little attention.

**Mercuric Ammonia.**—The mercuric salts react with ammonia to form compounds which may be grouped into three classes: first, those with ammonia of crystallization similar to salts with water of crystallization; second, ammono basic salts analogous to ordinary basic salts with  $NH_2$  in place of  $OH$  or either  $NH$  or  $N$  in place of  $O$ ; third, mixed aquo ammono basic salts containing both  $OH$  or  $O$  and  $NH_2$  or  $N$ .

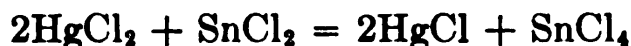
The first class with ammonia of crystallization may be prepared by the action of ammonia in the gaseous or liquid state upon mercuric salts, or by the action of aqueous ammonia upon these salts in the presence of ammonium salts. As examples of these compounds the following may be given:  $HgCl_2 \cdot 2NH_3$  [fusible white precipitate],  $HgCl_2 \cdot 12NH_3$ .

The second class, ammono basic mercuric salts, may be formed by the action of aqueous ammonia upon mercuric salts in the absence of ammonium salts. Examples of these salts are  $HgNH_2Cl$  [infusible precipitate], and  $Hg(NH_2)NO_3$ .

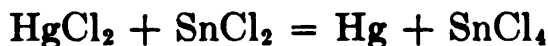
The third class, the mixed aquo ammono basic salts, are formed under conditions which are more favorable to hydrolysis than those for the two preceding classes. The compound  $Hg_2(OH)(NH)Cl$  may be cited as an example.

**Analytical Reactions of Mercury.**—Both the mercurous and mercuric ions are colorless, and the former is distinguished from all others by the fact that it will form a slightly soluble white precipitate of mercurous chloride with the chlorine ion which precipitate turns black when treated with ammonium hydroxide.

Both the mercuric and mercurous ions give mercuric sulfide with hydrogen sulfide in acid solution. This precipitate is insoluble in hot dilute nitric acid, but is dissolved by aqua regia. Mercuric salts are reduced by stannous chloride to mercurous salts or even metallic mercury as shown in the following equations,



and



When metallic copper is introduced into a solution of a mercury salt the copper is oxidized to copper as ion and the mercury ion is reduced to metallic mercury which forms a bright mirror-like coat on the remaining copper.

When the mercury salts are heated with lime or sodium carbonate, they give metallic mercury.

**General Relations of the Group.**—As is evident from the discussion given above, the members of the magnesium group do not form as close a family as do the members of the alkali and alkaline earth metals, but still there are some general relationships throughout the group. The increasing stability of the sulfides with increasing atomic weight is noticeable. Beryllium and magnesium sulfides are not formed in the presence of water even, while zinc sulfide is stable toward weak acids, but is not stable in contact with any but very dilute solutions of the strong acids. Cadmium sulfide is stable in the presence of dilute solutions of the strong acids, but is dissolved by concentrate solutions of them and by hot dilute solutions, while mercuric sulfide is stable even against boiling dilute nitric acid and is scarcely attacked by this acid in the concentrated state.

Beginning with zinc, the halogen compounds show a regular decrease in their degree of dissociation with increasing atomic weight both of the halogen and of the metal. The melting- and boiling-points of the members of the sub-group become lower as the atomic weights increase.

## CHAPTER XXIV

### COPPER, SILVER AND GOLD

**General.**—Copper, silver, and gold occupy the lower part of the right-hand column of Group I of the periodic system. From their position, they should bear some resemblance to the alkali metals, but from what has been learned concerning the relations between the members of the alkaline earth metals and magnesium sub-group it is evident that the resemblance need not be close. As a matter of fact the divergence is so great that it is necessary to search for points of resemblance. Perhaps the most striking point of similarity is that copper, silver and gold each forms a series of compounds in which it is monovalent. In addition copper forms another series in which it is divalent and gold one in which it is trivalent. The following table will give at a glance a comparison of the more prominent properties of the two sub-groups:

The Alkali Metals	The Copper Family
Low density 0.59–2.4.	High density 8.94–19.4.
Very active chemically.	Decidedly inactive.
Never occur free.	Often found free.
Halogen compounds are soluble.	Nearly all of the halogen compounds of the monovalent series are but slightly soluble.
Strong bases.	Weak bases, except silver.
Do not form complex ions.	Form many complex ions.

### COPPER

**History.**—Copper has been known from prehistoric times and since it is found free in nature in abundance, it was probably the first metal to be put to practical use by man. Before the extensive use of iron, tools were made of bronze, an alloy of copper and tin.

**Occurrence.**—Copper occurs in nature both free and in combination. The native copper is sufficiently abundant so that it

constitutes a very important ore as may be judged from the fact that the region in Michigan near Lake Superior produces from the native metal about one-sixth of the copper mined in this country per year. The compounds which are used as ores may be divided into two classes: the oxidized ores and the sulfide ores. The oxidized ores include cuprous oxide,  $\text{Cu}_2\text{O}$ , which is called cuprite or red oxide; cupric oxide,  $\text{CuO}$ , called melanconite or black oxide; and the basic cupric carbonates, malachite,  $\text{CuCO}_3$ ;  $\text{Cu}(\text{OH})_2$ , and azurite,  $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ . The sulfide ores include cuprous sulfide,  $\text{Cu}_2\text{S}$ , or chalcocite and the double sulfides of copper and iron known as chalcopyrite,  $\text{CuFeS}_2$ , and bornite,  $\text{Cu}_5\text{FeS}_4$ . The sulfide ores are the most important because from them this country produces about two-thirds of its output per year. The total production in 1915 was nearly 1,425,000,000 lb.

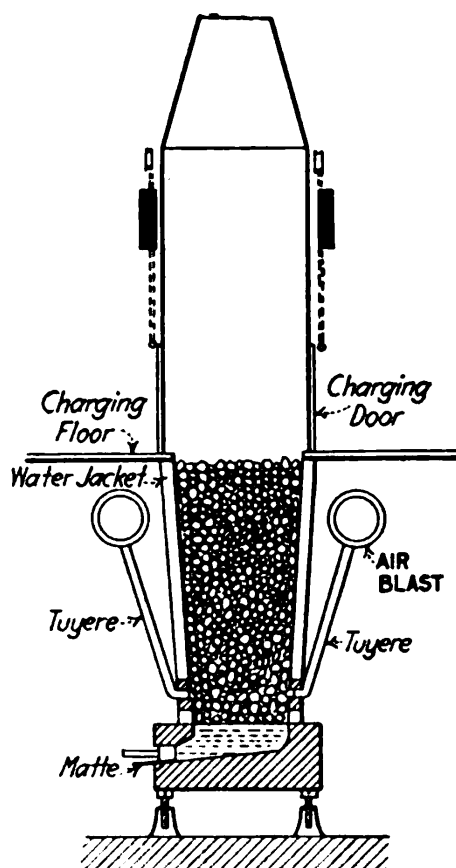


FIG. 59.

**Metallurgy.**—The method adopted for the extraction of copper from its ores naturally depends upon the substances present. If the copper is native, all that is necessary is to crush the rock and concentrate the copper by mechanical processes followed by melting in large reverberatory furnaces to separate the copper from the remaining gangue. If the ore is a sulfide it is crushed and concentrated by washing and flotation as described

under zinc. The latter process is so effective that from an ore running as low as 2 per cent. copper 90 to 96 per cent. of the metal can be obtained in the concentrate.

The first step involved in the actual smelting of the ore is the formation of a concentrated mixture of copper and iron sulfides known as copper matte. This is done by melting a properly proportioned mixture of the concentrated ore and limestone either in a reverberatory furnace, if the ore is in fine particles, or in a copper blast furnace if it is coarse. In either type of furnace,

part of the iron sulfide is oxidized to sulfur dioxide and iron oxide and the latter together with lime from the limestone and silica from the ore forms easily fusible silicates or slags, the remaining iron sulfide and the copper sulfide melt together forming the matte and when the charge is withdrawn from the furnace, the matte goes to the bottom of the receiving vessel and is easily separated from the slag. In the reverberatory furnace, the ore and limestone are spread on the horizontal bed of the furnace and exposed to the action of the flame produced by blowing powdered coal into the furnace with a blast of air; while in the copper blast furnace the ore and flux together with coke for fuel is charged

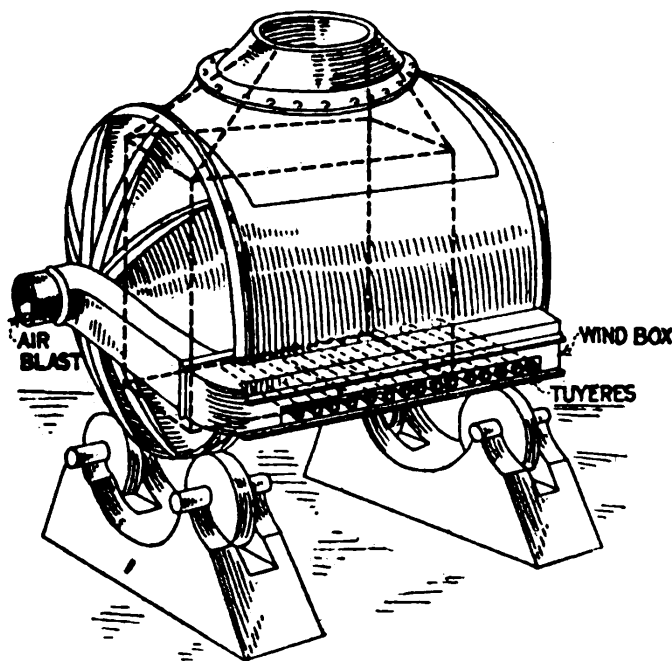
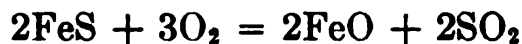


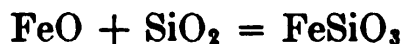
FIG. 60.

into the top of the long narrow vertical furnace (Fig. 59) into which air is blown at the bottom. The temperature reached is high and the molten slag and matte are drawn off at the bottom. The matte from either type of furnace is next treated in a copper converter (Fig. 60), which is a large, approximately barrel-shaped vessel resting on a rotating mechanism. The converter has a thick lining of magnesia,  $MgO$ . Air at a high pressure is blown into the converter from several blast pipes on the side.

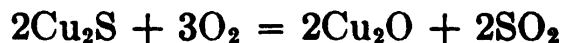
The large supply of air, oxidizes the ferrous sulfide in the matte to iron oxide and sulfur dioxide, thus liberating heat which serves to keep the mass fluid.



The sulfur dioxide escapes as gas, while the ferrous oxide combines with silica which is added along with the matte to form ferrous silicate slag,



Some cuprous sulfide is oxidized, but the cuprous oxide formed reacts at once with iron sulfide reforming cuprous sulfide,



After the iron has been eliminated the slag is poured off and the second period of blowing begins. The cuprous sulfide is now oxidized to some extent, forming cuprous oxide. This reacts with the remaining cuprous sulfide forming sulfur dioxide and metallic copper



At the completion of this operation metallic copper remains and this is poured into molds. It is known as blister copper and

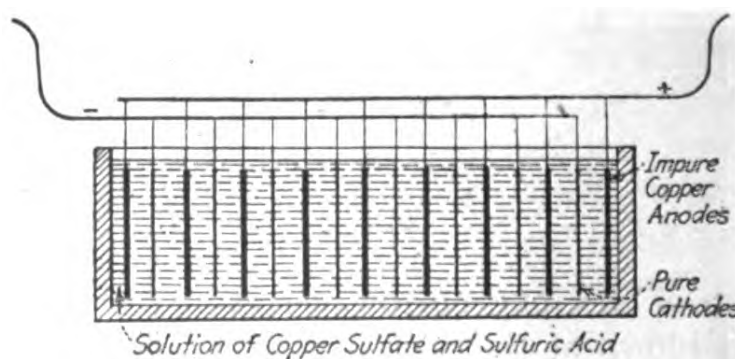


FIG. 61.

carries practically all of the nickel, gold, silver, and platinum that were in the original ore. It also contains some other impurities and is not fit to be used for most commercial purposes. Further purification is best obtained by means of electrolysis.

**Electrolytic Refining.**—For this process, the crude blister copper is cast into large plates which are used as anodes in electrolytic cells (Fig. 61) where the cathodes are thin plates of pure copper, and the electrolyte is an acidified solution of copper

sulfate. On passing a suitable current through the cells, copper is dissolved from the impure anodes and deposited in nearly pure condition on the cathodes. The impurities in the anode are either dissolved and held in solution in the electrolyte or remain undissolved and fall to the bottom of the cell. Gold, silver and platinum are thus precipitated and are recovered by subsequently melting up the slimes or mud from the bottom of the cells. The electrolytic copper so obtained is nearly pure. It is melted again, stirred with wooden poles to remove oxide and then cast into bars for the market.

**Physical Properties of Copper.**—Copper is red by reflected light and is one of the very few colored metals. When a very thin layer of copper is viewed by transmitted light it is bluish-green. The density of the metal is 8.94 and it melts at  $1,083^{\circ}$  and boils at  $2,310^{\circ}$ . The metal is a very good conductor of heat and only silver exceeds it in conductivity for electricity. A large proportion of the copper which is put upon the market is used for electrical conductors. For this purpose it must be extremely pure. It is highly malleable, ductile and tenacious, so it may be rolled or hammered into thin sheets or drawn into fine wire.

**Chemical Properties.**—Copper is not oxidized in perfectly dry air but in ordinary air it soon becomes coated with an adherent film of cuprous oxide and finally, especially if exposed to the weather, with a basic carbonate. The underlying metal is thoroughly protected by these films and is very durable. On this account, it is used for the roofs of important buildings and as a sheathing for ships. At somewhat elevated temperatures copper combines directly with oxygen, chlorine, and sulfur. It does not act on water at any temperature and is not dissolved by acids with evolution of hydrogen. This is connected with the fact that the cupric ion is a stronger oxidizing agent than the hydrogen ion. Such acids as contain elements in a condition which makes them stronger oxidizing agents than hydrogen as ion, nitric or hot concentrated sulfuric acid for example, will dissolve copper but with the reduction of the acid and not the evolution of hydrogen. On the other hand, when in contact with the air, acids like hydrochloric and even acetic dissolve the metal. The oxygen of the air is the oxidizing agent in this case.

The atomic weight of copper is 63.57.

**Alloys.**—Copper forms many varied and useful alloys with the other elements. With zinc it forms brass, 30 to 37 per cent. zinc, and tombac 2 to 15 per cent. zinc, and with zinc and iron, an alloy which is malleable when hot. Bronze contains essentially copper and tin, although other metals are often added, especially zinc. Gun metal contains 10 per cent. tin and bell metal from 17 to 20 per cent. tin. Speculum metal is one-third tin and contains a little arsenic. It takes a very high polish. Phosphor bronze contains tin and a little phosphorus. Aluminum bronze has from 3 to 10 per cent. of aluminum. That with the higher percentage of aluminum has about the color of gold, is easily cast, takes a high polish and is nearly as strong as cast steel. Manganese bronze has a content of about 30 per cent. manganese. Silicon bronze contains up to 5 per cent. silicon. It is sometimes used for exposed electric wires since its tenacity is greater than that of copper although its conductivity is smaller. German silver is an alloy of copper, nickel and zinc and usually contains about 22 per cent. each of zinc and nickel.

**Cuprous Compounds.**—The cuprous or monovalent compounds are formed as the first step in the oxidation of the element or in the reduction of the cupric, or divalent compounds. In some ways many of them are more stable than the cupric compounds, and are formed from the latter by spontaneous decomposition; but in general they are relatively unstable and are transformed by oxidizing agents into the cupric compounds. The principal cuprous compounds are  $\text{Cu}_2\text{O}$ ,  $\text{CuCl}$ ,  $\text{CuBr}$ ,  $\text{CuI}$ ,  $\text{CuNC}$ , and  $\text{Cu}_2\text{S}$ . Some of the cuprous oxyacid salts can be obtained in solution, but they soon decompose in such a manner that half the cuprous is reduced to metallic copper while the other half is oxidized to cupric. The cuprous ion  $\text{Cu}^+$  seems to be incapable of existing in any appreciable concentration for all the soluble stable salts are those of complex ions.

When a given quantity of electricity is passed through a cuprous salt, just twice as much copper is deposited as when the same quantity is passed through a cupric solution. This of course, would follow from the relation between their valencies.

**Cuprous Oxide.**—Cuprous oxide occurs in nature and is known as cuprite or red oxide of copper. It may be prepared

the direct union of the elements, or by the reduction of an alkaline solution of a cupric salt with glucose. It has a red color and is not soluble in water. It dissolves in hydrochloric acid forming the compound,  $\text{HCuCl}_2$  which gives the complex ion  $\text{CuCl}_2^-$ ; and in ammonium hydroxide owing to the formation of the complex ion  $\text{Cu}(\text{NH}_3)_2^+$ . Both of these ions are colorless. Cuprous hydroxide is not stable.

**Cuprous Chloride.**—Cuprous chloride,  $\text{CuCl}$ , is one of the most important of the cuprous salts. It is most readily prepared by adding hydrochloric acid to a solution of cupric chloride,  $\text{CuCl}_2$ , and boiling for some time with finely divided copper out of contact with air. The equation for the reaction is:



When the solution is poured into water, the compound  $\text{HCuCl}_2$  breaks up,



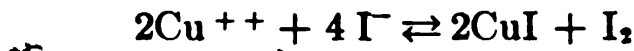
Cuprous chloride is white and is but slightly soluble in water. It is dissolved by concentrated hydrochloric acid and soluble chlorides in general through the formation of the complex ions  $\text{CuCl}_2^-$  or  $\text{CuCl}_3^-$ . These solutions are colorless when pure, but quickly become colored when exposed to the air, owing to the oxidation to cupric compounds. Cuprous chloride is also soluble in ammonium hydroxide solutions owing to the formation of the colorless ion  $\text{Cu}(\text{NH}_3)_2^+$ . The solution, however, quickly turns blue upon exposure to the air because of oxidation to the highly colored cupric ammonia ion.

Both the ammoniacal and hydrochloric acid solutions of cuprous chloride have the property of absorbing carbon monoxide through the formation of an unstable compound. Advantage is taken of this in gas analysis.

**Cuprous Bromide.**—Cuprous bromide,  $\text{CuBr}$ , is very similar to the chloride. It may be prepared by simply heating the anhydrous cupric bromide out of contact with the air when it decomposes into bromine and the cuprous salt. The chloride shows a tendency in the same direction but the decomposition is incomplete.

**Cuprous Iodide.**—Cupric iodide is so unstable that it decomposes at ordinary temperatures even when in solution; so when

a soluble iodide is added to a solution of a cupric salt, cuprous iodide is at once precipitated and iodine liberated,



The cuprous iodide is colorless but appears brown from the color of the liberated iodine. The reaction is reversible and is far from complete unless the iodine is reduced by the addition of a sulfite or other suitable reducing agent.

**Cuprous Cyanide.**—When potassium cyanide is added to a cupric salt, cupric cyanide is precipitated; but this is unstable and soon decomposes into the cuprous cyanide,  $\text{CuNC}$ , and cyanogen,



The cuprous cyanide is practically insoluble in water, but dissolves readily in an excess of potassium cyanide owing to the formation of the colorless very stable complex anion  $\text{Cu}(\text{NC})_5^-$ . This ion gives an exceedingly low concentration of copper as ion, so low in fact, that it does not show the properties of copper as ion and will not give a precipitate of copper sulfide (which see) with hydrogen sulfide. Because of the very small concentration of the copper ion from this cuprocyanogen ion, all the slightly soluble salts of copper will dissolve in an excess of potassium cyanide.

**Cuprous Sulfide.**—Cuprous sulfide,  $\text{Cu}_2\text{S}$ , is formed by heating the cupric compound in a stream of hydrogen. It is found in nature and is then known as copper glance. It is dark colored and is not soluble in water or cold dilute acids, but is dissolved by hot dilute nitric acid and by potassium cyanide.

**The Cupric Compounds.**—The cupric compounds are divalent and are in general more common and more important than the cuprous. The halogen compounds, as noted in the discussion of the cuprous salts, show a marked tendency to pass over into the cuprous salt and the free halogen. On the other hand, the only stable oxy salts of copper belong to the cupric series. When in dilute solution in water, the cupric salts all show a blue color which consequently is said to be the color of the cupric ion,  $\text{Cu}^{++}$ . When an excess of ammonium hydroxide is added to a cupric salt, the precipitate of cupric hydroxide or basic salt which

first formed is redissolved and the solution becomes intensely blue. Such a solution acts as though it contained a complex cupric ammonia ion,  $\text{Cu}(\text{NH}_3)_4^{++}$ , having a deep blue color.

**Cupric Oxide and Hydroxide.**—Cupric oxide or black oxide of copper,  $\text{CuO}$ , occurs in nature in the ore melaconite. It may be prepared by heating the metal in a stream of oxygen or air; cuprous oxide is first formed. When heated to redness, it acts as a good oxidizing agent toward hydrogen and organic substances, oxidizing them to water and carbon dioxide and being itself reduced to metallic copper. This property is employed in the quantitative synthesis of water and in the analysis of organic compounds. Copper oxide is also used in the refining of petroleum to remove sulfur compounds.

Cupric hydroxide,  $\text{Cu}(\text{OH})_2$ , is a weak base which is but slightly soluble in water. It is precipitated as a light blue gelatinous substance when a soluble hydroxide is added to a cupric salt. Upon standing or more quickly when the solution is boiled, it becomes black and is transformed into a hydrated form of the oxide.

Cupric hydroxide is of course soluble in acids. It is not dissolved by sodium hydroxide of moderate concentrations, but is soluble in ammonium hydroxide owing to the formation of the deep blue complex cupric ammonia ion  $\text{Cu}(\text{NH}_3)_4^{++}$ . It is also soluble in solutions of sodium and potassium tartrate, especially in the presence of sodium hydroxide, a complex copper tartrate ion,  $\text{CuC}_4\text{H}_2\text{O}_6^{--}$ , is formed. This solution is deep blue like the ammoniacal solution, and is used in the determination of glucose since the latter reacts in a definite manner with it forming cuprous oxide which is precipitated. It is called Fehling's solution. This solution of cupric hydroxide in ammonia has the remarkable property of dissolving cotton or other forms of cellulose. This is reprecipitated upon acidulating the solution in a form having a silky luster. This is the basis of the process of making artificial silk.

**Cupric Chloride.**—Cupric chloride,  $\text{CuCl}_2$ , may be prepared by the direct union of its elements or by the interaction of hydrochloric acid with the oxide, hydroxide, or carbonate.

Anhydrous cupric chloride is yellow, a dilute solution of the salt is blue and a concentrated solution is green, perhaps because

of the simultaneous presence of the ion and of the undissociated salt. From the concentrated solution, the blue hydrate,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , crystallizes out.

The deep blue solution formed by the addition of an excess of ammonia to a solution of cupric chloride deposits upon concentration crystals having the formula  $\text{Cu}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$ . The anhydrous chloride will combine directly with ammonia to form the compounds,  $\text{CuCl}_2 \cdot 6\text{NH}_3$  and  $\text{CuCl}_2 \cdot 2\text{NH}_3$ , these are analogous to salts with water of crystallization.

**Cupric Sulfate.**—Copper sulfate or blue vitriol,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , is the most important copper salt. It may be made on a small scale by heating copper with concentrated sulfuric acid. The sulfuric acid here acts as the oxidizing agent, and is itself reduced to sulfur dioxide,



On a large scale, it is made by carefully oxidizing naturally occurring sulfides by roasting them in the air and dissolving out the sulfate with water, or by roasting the ores or matte and dissolving in dilute sulfuric acid. The salt is soluble in water, and crystallizes from solution as the blue pentahydrate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . The five molecules of water of crystallization in the pentahydrate may be successively replaced by the same number of molecules of ammonia. A similar thing is true for other salts and serves to strengthen the resemblance between ammonia and water. With potassium sulfate, copper sulfate forms the double salt,  $\text{CuSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , isomorphous with the corresponding magnesium compound.

Copper sulfate is used in the preparation of other copper compounds, in calico printing, in the purification of copper by electrolysis, in electroplating and electrotyping, as a germicide and fungicide (mixed with slaked lime it forms Bordeaux mixture). Since it is very poisonous to the lower orders of plants, it is used extensively to destroy such organisms as often give to public water supplies a disagreeable taste and odor. It is used in making the electric cell known as the Daniel's battery and also in the gravity battery.

**Cupric Nitrate.**—Copper nitrate,  $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is a blue salt which may be made by dissolving the metal, the oxide or

carbonate in nitric acid. It is very easily soluble in water. When heated it gives the oxide.

**Cupric Carbonate.**—Cupric hydroxide is such a weak base that the normal carbonate does not seem to be able to exist since it has neither been found in nature nor prepared in the laboratory. Two basic carbonates, malachite,  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$  and azurite,  $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$  occur fairly abundantly in nature and are valuable copper ores. The green coating which gradually forms on copper exposed to the weather has the composition of malachite.

**Cupric Acetate.**—A basic copper acetate, known as verdigris having a fine bluish-green color and used as a pigment, is formed by the action of the air and of the crudest kind of vinegar (acetic acid) upon plates of copper. The oxygen of the air is the oxidizing agent in this case. The normal salt,  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$  may be obtained by crystallization from dilute acetic acid. It forms dark green crystals and is used as a pigment.

**Cupric Sulfide.**—When hydrogen sulfide is passed through a neutral or acid solution of a cupric salt, a brownish-black precipitate is thrown down; this consists principally of the cupric sulfide,  $\text{CuS}$ , but always contains some cuprous sulfide,  $\text{Cu}_2\text{S}$ . By drying this precipitate and heating it in a current of hydrogen, it is completely transformed into the cuprous compound. The hydrogen assists by sweeping away the sulfur.

Cupric sulfide is practically insoluble in cold dilute acids, but dissolves in hot dilute nitric acid. In the latter case, hydrogen sulfide is not evolved; but the sulfur as ion is oxidized to free sulfur and the nitric acid reduced to nitric oxide.

**Copper Ferrocyanide, Osmotic Pressure.**—Copper ferrocyanide,  $\text{Cu}_2\text{Fe}(\text{NC})_6$  has a very intense brownish-red color and is exceedingly slightly soluble. Because of these properties, it is of some importance to analytical chemistry. It is, however, of far greater importance to biology and to theoretical chemistry, because of the part which it plays in the study of the phenomena of osmotic pressure.

Copper ferrocyanide is a colloidal substance, and may be obtained as a membrane filling the pores of a porous cell (Fig. 62) by putting a solution of copper sulfate on the inside of the cell and a solution of potassium ferrocyanide on the outside and

allowing the whole to stand for some time. The ferrocyanide is precipitated in the pores of the cell where the two solutions meet. After this cell has been thoroughly washed to free it from soluble salts, it behaves in a very peculiar manner. Pure water will pass through it in either direction very much as through an ordinary porous cell only more slowly; but if a solution of sugar or of many other substances is placed in the cell, and the latter then set into a dish of pure water, the water will be drawn through

into the solution. If the cell be closed with a cork, the water will continue to enter until it has produced a certain pressure which can be measured upon an attached manometer. When this pressure is reached, the water ceases to enter, and if by any means the pressure within the cell is increased *pure water and not solution* is forced out of the cell until the pressure is reduced to its former value. This pressure at which there is equilibrium between pure water and a solution separated by a membrane such as copper ferrocyanide is called the osmotic pressure of the solution.

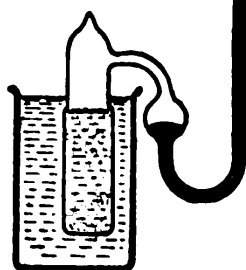


FIG. 62.

When the conditions which affect the osmotic pressure are investigated, it is found that for fairly dilute solutions, the osmotic pressure is directly proportional to the concentration of the solution and to the absolute temperature at which it is measured. In these ways it corresponds exactly to the pressure of a gaseous substance. *In fact, the osmotic pressure of a solution is the same as the pressure which the solute would have if it were in the state of a gas and occupied the*

*volume of the solvent in which it is dissolved at the temperature at which the osmotic pressure is measured.* The gas law equations,  $PV = K$  and  $V = K'T$  apply to osmotic pressure also,  $P$  is the osmotic pressure,  $V$  the volume of the solvent (not the volume of the solution), and  $T$  the absolute temperature. The osmotic pressure of a solution containing one gram mole in a liter of solvent is approximately 22.4 atmospheres at  $0^{\circ}\text{C}$ .

Other membranes than copper ferrocyanide may be used

without altering the value of the osmotic pressure of a solution provided always that they will permit the solvent to pass through, but not the solute. Such membranes are called semipermeable membranes. They seem to act as selective solvents and to dissolve the solvent but not the solute of the main solution.

The osmotic pressure of salt solutions is abnormally high having about twice the calculated value, in the case of sodium chloride, for example. The significance in connection with the dissociation hypothesis is obvious, but really it adds nothing to the evidence already given in favor of this theory, because the science of thermodynamics has shown that the osmotic pressure of a solution is directly proportional to the relative lowering of the vapor pressure of the solution and hence to the lowering of the freezing-point and to the rise in the boiling-point. If these are abnormal, as they are, for salts, the osmotic pressure must be abnormal also.

The osmotic pressures of concentrated solutions are by no means small and pressures up to 36 atmospheres have been measured. Such a pressure is equal to that exerted by a column of water 1,200 ft. in height. And this enormous pressure it must be remembered, is produced simply by the water's passing through a semipermeable membrane into a solution without the action of any external force.

Many of the processes which take place in the living organisms are at least partially osmotic in their nature, the movement of sap in plants and of the bodily fluids in animals, for example.

**Analytical Properties of Copper.**—In analysis, use is most frequently made of the following properties: namely, the sulfide is but slightly soluble in water and cold dilute acids, but soluble in hot dilute nitric acid (separation from mercury); the sulfate is soluble in water (separation from lead); the hydroxide is soluble in an excess of ammonia (separation from bismuth); and the sulfide is soluble in potassium cyanide (separation from cadmium). The intense blue color of the cupric ammonia ion which is formed by the addition of an excess of ammonium hydroxide to the cupric salt is fairly characteristic, since nickel is the only other metal which has similar properties. A very characteristic test for copper is based on the fact that metallic iron will precipitate bright metallic copper upon its

to the product of the volts times the coulombs, it follows that the potential or electromotive force of a cell is equal to the free energy produced during 1 gm. equivalent of change divided by 96,500. Expressed in the form of an equation,

$$\text{E.m.f.} = F/96,500$$

in which e.m.f. stands for electromotive force, and  $F$  for the free energy of 1 gm. equivalent of chemical change. From this, it follows that the potential of a cell is directly proportional to the decrease in the free energy accompanying the transformation of a gram equivalent of the oxidizing and reducing agents in the cell. Since this free energy is different for different combinations, the potentials of various cells are quite dissimilar. Oxidizing agents can be arranged in the order of their activity, *i.e.*, the decrease in the free energy involved in the transformation of a gram equivalent, and a number can be assigned to each which represents the potential of an electrode in the normal ionic solution<sup>1</sup> of the oxidizing agent. This number may be represented by  $E$  and then,  $E = F'/96,500$ ; where  $F'$  is the free energy produced when 1 gm. equivalent of the oxidizing agent is reduced. The following table gives a short list of oxidizing agents arranged in the order of their oxidizing power, and also gives the value of  $E$ . This table is a part of what is called the potential series.

Agent	E in volts	Agent	E in volts
$\text{NO}_3^-$ .....	+ 1.75	$\text{H}^+$ .....	+ 0.277
$\text{Cl}_2$ .....	+ 1.694	$\text{Pb}^{++}$ .....	+ 0.129
$\text{O}_2$ .....	+ 1.396	$\text{Ni}^{++}$ .....	+ 0.049
$\text{Br}_2$ .....	+ 1.270	$\text{Co}^{++}$ .....	+ 0.045
$\text{Ag}^+$ .....	+ 1.048	$\text{Tl}^+$ .....	- 0.045
$\text{Hg}^+$ .....	+ 1.027	$\text{Fe}^{++}$ .....	- 0.063
$\text{Cu}^{++}$ .....	+ 0.606	$\text{Cd}^{++}$ .....	- 0.143
		$\text{Zn}^{++}$ .....	- 0.493

A + sign before the value of  $E$  indicates that the electrode is

<sup>1</sup> A normal ionic solution is one which contains in a liter such a quantity of the salt that there will be 1 gm. equivalent of the ion present in the actually dissociated state. Because of the incomplete dissociation, such a solution will contain per liter more than one equivalent of the salt.

**positive** against the solution of that oxidizing agent, and a **— sign** means that the electrode is negative toward the solution, **and** the significance of a negative sign is that free energy is taken **up** instead of being given out when the ion is changed to the **metal**. This is the case with all the metals which are hard to **reduce** from their compounds.

Any oxidizing agent in this list is able to form anything **lying** below it and is formed by all that stand above. For **example**, the cupric ion will oxidize anything from hydrogen to **zinc** and change it from the element to the ion, while copper is **itself** oxidized by mercury and all that stand above to the cupric ion. A voltaic cell then may be made up of a combination of any **two** of these agents, and its electromotive force will be the **algebraical** difference between the value of  $E$  for the two electrodes. For example, a cell might be made up of a silver electrode in a silver solution and a copper electrode in a copper solution, and it would have an e.m.f. of  $1.048 - 0.606 = 0.442$  volts. The silver electrode would be positive toward the copper and the latter would dissolve, while metallic silver would be deposited. The electromotive force of the Daniell cell may be calculated from this table by subtracting the value of zinc,  $-0.493$  from that of copper,  $+0.606$ ;  $0.606 - (-0.493) = 0.606 + 0.493 = 1.099$  volts. Here in contrast to the above, the copper is positive toward the zinc and is deposited while the zinc dissolves.

The activity of an oxidizing agent depends upon the concentration. The figures given above apply to normal ionic solutions containing 1 gram. equivalent of "actual ion" per liter; in more dilute solutions, the electrodes are less positive if the oxidizing agent is a cation. Anything which tends to reduce the concentration of the copper ion for instance, will tend to bring the potential of the copper electrode nearer the zinc and reduce the potential of the copper zinc cell. The concentration of copper in a solution containing an excess of ammonia is very small, and the potential of a cell made up of a copper electrode in such a solution and a zinc electrode in zinc sulfate solution is much smaller than that of the Daniell cell. If potassium cyanide is used instead of the ammonia, the concentration of the copper is still further reduced, so that the potential of the copper elec-

trode is actually made smaller than that of the zinc; and in a cell made up of the two, the processes which take place in the Daniell cell are reversed, copper going into solution and the zinc being deposited.

### SILVER

**General.**—Because of its occurrence free in nature, silver has been known and used from prehistoric times. Its relationship to the other elements is rather complex as will be seen by a study of its compounds. Physically it is much like copper aside from the difference in color; chemically it is like mercury in the mercurous, and copper in the cuprous states in that it is monovalent and also in the slight solubilities of its halogen compounds. It differs radically though from both mercury and copper in that its hydroxide is a strong base, and that its soluble salts of strong acids are neutral. In this it resembles the alkali metals, and some of its salts are isomorphous with the corresponding salts of potassium. The silver ion  $\text{Ag}^+$  is a good oxidizing agent, and the metal is obtained very easily from many of its compounds. The oxide for example, when heated, acts like mercuric oxide in that it is changed into the metal and oxygen. Scheele took advantage of this in one of his methods for the preparation of oxygen.

**Occurrence.**—Like copper, silver is found in nature both free and in combination. The native silver is a fairly important ore, but is practically never found pure, being alloyed with gold, copper or mercury. The most important ore is the sulfide  $\text{Ag}_2\text{S}$  called argentite or silver-glance. This is usually found in isomorphous mixture with lead sulfide. In addition there are compounds of silver sulfide and antimony or arsenic sulfides known as pyrargyrite  $\text{Ag}_3\text{SbS}_3$ , and proustite,  $\text{Ag}_3\text{AsS}_3$ .

**Metallurgy.**—The metallurgy of silver is complicated by the fact that it is generally associated with other metals such as copper, lead, zinc and gold which it is necessary and desirable to extract at the same time. To meet the needs of individual cases, a considerable variety of methods for extracting the silver have been devised. These may be grouped into smelting or dry processes, amalgamating and leaching or wet processes. The smelting methods are usually applied to ore which contains relatively more copper or lead than silver. If they are mainly

copper ores, they are worked as described under that metal, and the blister copper obtained will carry practically all the silver in the ore. This crude copper is then purified by electrolysis, and the silver is obtained in the anode mud. The lead ores are smelted as will be described under that metal, and the lead will contain the silver. This is called work lead or base bullion. The silver is removed from this by what is known as the Parke's process which is as follows: Work lead is melted in large kettles and kept molten for some time to allow other impurities to be oxidized and skimmed off as "dross." Then a quantity of zinc equal to from 0.5 to 2.0 per cent. of the weight of the lead is stirred into the molten mass. Zinc and lead are only slightly soluble in each other, while zinc is a much better solvent for silver than lead is. The zinc, therefore, acts as an extractive solvent, and dissolves the greater part of the silver (see the Law of Distribution) from the lead. The silver zinc alloy being much the lighter, rises to the surface, and on being allowed to cool, forms a solid crust while the lead is still molten. This is skimmed off and freed from most of the lead which adheres to it, and the zinc is then distilled from the alloy in large graphite retorts. The silver is heated in a cupellation furnace where any lead which it retains is oxidized to litharge,  $\text{PbO}$ , and absorbed in the bone ash which forms the bottom of the furnace. The silver remains unoxidized, accompanied by any gold that was in the original bullion. These are separated by dissolving the silver in hot concentrated sulfuric acid; the gold is left unchanged. The silver is precipitated from the silver sulfate solution by means of metallic copper.

There are also electrolytic processes for getting silver and gold from work lead. The silver and gold are found in the residues in the bottom of the cell.

**Amalgamation Process.**—This depends upon the solution of free silver from an ore in metallic mercury, forming silver amalgam. After separating this from the ore gangue, it is freed from excess mercury by straining through canvas or buckskin. The solid amalgam is then distilled in an iron retort, the mercury passing over and the silver remaining in the retort. This process is applicable to ore in which the silver is either free or can be easily reduced to the free state.

**The Halogen Compounds of Silver.**—Silver fluoride may be made by the action of hydrofluoric acid upon the oxide or carbonate. It is highly soluble in water and is deliquescent.

The chloride, bromide, and iodide of silver are very slightly soluble in water or in dilute acids, and are thrown down as curdy precipitates upon the addition of the corresponding halogen salts to a solution of a silver salt. The chloride is white and soluble to the extent of 0.002 grm. per liter of water. The bromide has a pale yellow color and is less soluble than the chloride. The iodide is distinctly yellow, and is the least soluble of the three. When exposed to the light, silver chloride and bromide darken and some free halogen is formed together with a subchloride or bromide,  $\text{Ag}_2\text{Cl}$  or  $\text{Ag}_2\text{Br}$ . Silver iodide is unchanged in the light unless an excess of  $\text{AgNO}_3$  is present. These facts are important in connection with photography (p. 384).

The silver halides at ordinary or lower temperatures will combine directly with ammonia for the formation of the following compounds,  $2\text{AgCl}\cdot 3\text{NH}_3$ ,  $\text{AgCl}\cdot 3\text{NH}_3$ ,  $\text{AgBr}\cdot \text{NH}_3$ ,  $2\text{AgBr}\cdot 3\text{NH}_3$ ,  $\text{AgBr}\cdot 3\text{NH}_3$ ,  $2\text{AgI}\cdot \text{NH}_3$ ,  $\text{AgI}\cdot \text{NH}_3$ .

Silver chloride is fairly soluble in concentrated solutions of hydrochloric acid and of the easily soluble chlorides, apparently because of the formation of the ion  $\text{AgCl}_2^{--}$ . It is also easily soluble in ammonium hydroxide owing to the formation of the stable complex ion,  $\text{Ag}(\text{NH}_3)_2^+$  called the silver ammonia ion. Silver bromide is somewhat soluble in ammonium hydroxide, but the iodide is scarcely affected. The explanation is that silver bromide because of its slight solubility gives a concentration of silver as ion in the solution which is but little higher than that of the silver ion which together with the ammonia is in equilibrium with the complex silver ammonia ion, so its concentration cannot be much reduced through the formation of this ion. Silver iodide is still less soluble, and the concentration of the silver ion in its solution is smaller than that from the silver ammonia ion.

Sodium thiosulfate interacts with silver salts for the formation of the complex crystalline salt,  $2\text{NaAgS}_2\text{O}_3\cdot \text{Na}_2\text{S}_2\text{O}_3$ . When in solution, this seems to give the complex ion,  $\text{AgS}_2\text{O}_3^-$ . The concentration of the silver as ion from this seems to be about the same as that from silver iodide for sodium thiosulfate does

not have much effect upon the latter although it dissolves silver bromide with ease.

**Silver Cyanide.**—Soluble cyanides give with the soluble silver salts a precipitate of silver cyanide which is somewhat less soluble than the chloride. The cyanide is soluble in ammonium hydroxide and very easily in an excess of potassium cyanide owing to the formation of the very stable complex silver cyanogen ion,  $\text{Ag}(\text{NC})_2^-$ , similar to the complex cuprocyanogen ion,  $\text{Cu}(\text{NC})_2^-$ . The concentration of the silver ion from this ion is so very small that silver iodide, and all of the other difficultly soluble salts of silver, are dissolved by potassium cyanide in excess. The sulfide requires the largest excess.

Solutions of this potassium silver cyanide are used in silver electroplating. The object to be plated is made the cathode and a plate of pure silver the anode.

**Silver Nitrate.**—Silver nitrate,  $\text{AgNO}_3$ , is the most important salt of silver. It is made by the action of nitric acid upon the metal;



Silver nitrate is a white crystalline easily soluble salt, isomorphous with potassium nitrate. It melts at a temperature a little over  $200^\circ$  and when cast in sticks is sometimes used in medicine as a caustic under the name of lunar caustic. Its use as a caustic depends upon the property of rendering insoluble certain nitrogenous substances, called the albuminoids.

In the pure state, it is not altered by light; but in the presence of reducing agents, it is changed to finely divided metallic silver having a black color. This is the cause of the stains which it produces on the skin. The nitrate is much used in the laboratory for the detection and estimation of the halogens and is also the starting-point for the preparation of most of the other silver salts.

**Silver Sulfate.**—Silver sulfate may be made by the action of hot concentrated sulfuric acid upon the metal;



Advantage is taken of this reaction in the "parting" of the alloys of gold and silver which are obtained in the smelting and refining

of these metals. The silver is dissolved while the gold is not. It is moderately soluble in water and will combine with aluminum sulfate forming the alum  $\text{AgAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , which is isomorphous with the corresponding potassium salt and with the whole series of alums.

**Silver Sulfide.**—Silver sulfide,  $\text{Ag}_2\text{S}$ , is so very slightly soluble that it is formed by the action of hydrogen sulfide upon all silver compounds except the complex potassium silver cyanide in the presence of a very large excess of potassium cyanide. It is even formed, as noted above, by the action of hydrogen sulfide or of other sulfides upon metallic silver.

**Silver Carbonate.**—Silver carbonate,  $\text{Ag}_2\text{CO}_3$ , is a pale yellow salt slightly soluble in water to which it imparts a faint alkaline reaction. It resembles lithium carbonate in that it is more soluble in the presence of carbon dioxide. The fact that the normal salt exists indicates that silver hydroxide is a strong base.

**Other Salts.**—Silver thiocyanate,  $\text{AgNCS}$  (white), silver chromate,  $\text{Ag}_2\text{CrO}_4$  (red), silver arsenite,  $\text{Ag}_3\text{AsO}_3$  (yellow) and silver arsenate,  $\text{Ag}_3\text{AsO}_4$  (reddish-brown) are a few of the salts which are used in analysis.

**Photography.**—The most important of the modern photographic processes depend upon the sensitiveness of the silver halides toward light. The "dry plate" upon which the picture is originally taken consists of a plate of glass or a film of celluloid covered with a dried emulsion of silver bromide in gelatine.

When such a plate is exposed for a fraction of a second to light, no visible action takes place; but if it is then placed in a suitable reducing agent called the "developer," the portions of the silver bromide which were exposed to the light are reduced to metallic silver at a rate which is proportional to the intensity of the light and the time of exposure. The reduced silver is deposited as a black substance in the very position of the bromide from which it was obtained. The unexposed bromide will also be reduced by the developer but very much more slowly than that which has been acted upon by light. If the exposure was made in a camera, there will be developed upon the plate an image which in its light and shade effects is the reverse of the object, that is, it will be dark where the object is light. This is called the negative. After the plate is "developed," it has then to be "fixed;" that

to say, the unchanged silver bromide must be removed so that the plate may not be further acted upon by the light. This is done by taking advantage of the solubility of the bromide in sodium thiosulfate or "hypo" as it is often called.

Just why the bromide which has been exposed to light is more easily reduced than the unexposed is not known with certainty, but it may be connected with the fact that light will transform it into a subbromide as noted above.

From the negative, "positives" or "prints" are made by allowing light to pass through the negative and strike sensitized paper which is placed in direct contact with the gelatine film of the negative. The dark portions of the negative which correspond to the light portions of the object protect the paper from the action of light, and when the print is finished it will be light just where the object was. Some printing-out papers are sensitized with silver bromide and these require only very brief exposure, but must be developed like plates. Others contain silver chloride and the printing is continued until the image is plainly visible upon the paper. Such prints are then "toned" by treating them with a solution of sodium chloraurate,  $\text{NaAuCl}_4$ , sodium gold chloride as it is called. The silver which has been reduced by the light, in turn reduces the gold to metallic gold which in the finely divided state has a pleasing reddish tint. By replacing the gold solution by potassium chlorplatinate,  $\text{K}_2\text{PtCl}_6$ , platinum will be precipitated instead of gold, giving a very dark tone. By whatever process made, the prints after development or toning must be fixed by dissolving out the unchanged silver salts with sodium thiosulfate.

**Mirrors.**—Mirrors are now usually made by coating glass with silver. This is done by the action of reducing agents such as the tartrates, glycerine, formaldehyde, or a reducing sugar upon ammoniacal solutions of silver nitrate. These mirrors are far superior to the old-fashioned ones which were backed with an amalgam of tin.

**Analytical Properties of Silver.**—The silver ion is colorless, and forms a difficultly soluble compound with the chlorine ion, a property which is also possessed by the mercurous, cuprous, and lead ions. Analytically, the cuprous compounds are unimportant. Silver chloride is not soluble in hot water, a distinction

from lead chloride; but is soluble in ammonium hydroxide, a distinction from mercurous chloride. In quantitative analysis, silver is usually weighed as the chloride, but often as the metal, which is obtained either by electrolysis or by oxidizing all the other metals, except gold and platinum, in the air at a high temperature and weighing the metallic bead which is so obtained, then dissolving out the silver with nitric acid or sulfuric acid and weighing the residue of gold and platinum. The difference in weight is the weight of the silver.

### GOLD

Gold has been known from prehistoric times. From its striking appearance and its occurrence free in nature it must have been among the earliest of the metals to attract the attention of men.

Gold forms a comparatively small number of compounds since all of its simple salts with the oxyacids are very unstable. In fact, gold seems to be practically incapable of existing as a simple ion although several complex ions are known. The compounds of gold belong to two series, the aurous in which the gold is monovalent and the auric in which it is trivalent. These compounds are characterized by the great ease with which they decompose to give metallic gold. This, in general, may be brought about by comparatively feeble reducing agents or by a moderate rise in temperature. The simple aurous halogen compounds are not soluble in water and this establishes a sort of relationship with copper and silver.

**Occurrence.**—Gold generally occurs free in nature, its only native compounds being those with tellurium. Native gold is rarely found pure, being almost always alloyed with silver. It is carried in finely divided conditions in quartz and other rock materials and in pyrite, galena and other sulfides. It may be found in its original deposits in veins running through the main rock masses or in alluvial beds of sand or gravel formed by the breaking down of the original deposits through weathering action. Gold in deposits of the former kind is called reef gold while that of the latter kind is called placer gold.

Among the minerals containing gold and tellurium, sylvanite,  $(\text{AuAg})\text{Te}_2$  and calaverite,  $\text{AuTe}_2$  may be mentioned. These

minerals are much less frequently found than native gold, but are of importance in some gold districts.

**Metallurgy.**—The processes for extraction of gold may be classified like those for silver as smelting, amalgamation, and leaching processes; but for gold there is an additional class, simple washing processes.

In the latter, gold in placer deposits of sand or gravel is concentrated by shaking up the material with water and allowing the gold to separate by its greater density from the lighter sands. These methods do not save all of the gold even when carried out under good conditions, and hence are used chiefly by prospectors, and in the opening up of new gold fields. They are greatly increased in efficiency if mercury is used to collect the concentrated gold as an amalgam and in this form they are rather widely used.

**Amalgamation Processes.**—Amalgamation processes for gold are very similar to those used for silver, and gold and silver are frequently recovered in the same operation. If the gold is disseminated in quartz or other massive rock the metal is recovered by crushing the ore in stamp mills and leading the crushed material over amalgamated plates, *i.e.*, copper plates coated with mercury. The gold is held by this mercury, and from time to time the gold amalgam is scraped from the plate; excess mercury is removed by filtering the amalgam through canvas or buckskin and the resulting solid amalgam is distilled to free the gold from mercury.

**Smelting Processes.**—Gold in copper or lead ores is concentrated during the smelting of these ores into the blister copper or the work lead. It is removed from these products, along with silver by the refining processes already described under silver and copper.

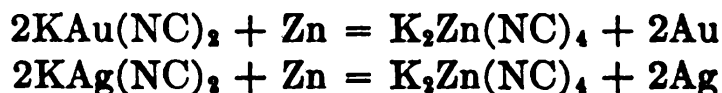
When both gold and silver are thus obtained, a separation or “parting” is necessary. A common method of doing this is to treat the gold-silver alloy with boiling concentrated sulfuric acid. Silver dissolves almost completely while gold is unaffected. The gold, after removal of silver sulfate solution, is melted, refined and cast into bars. Electrolytic processes are also used.

**Leaching Processes.**—The most important wet methods for gold extraction are the *amalgamation* and the *cyanide processes*.

In the former, finely crushed gold ore containing the free metal is treated with a solution of chlorine in water. This dissolves gold, forming gold chloride,  $\text{AuCl}_3$ . From the solution, gold is precipitated as the sulfide by means of hydrogen sulfide.

The *cyanide* process, patented in 1890 by McArthur and Forrest, is very widely used for the treatment of low grade ores that cannot be profitably worked by smelting. It is carried out by allowing the crushed ore to remain in contact for a considerable time with a very dilute solution of potassium cyanide,  $\text{KNC}$ . The solution dissolves both gold and silver from the ore forming potassium aurocyanide,  $\text{KAu}(\text{NC})_2$ , and potassium argenticyanide,  $\text{KAg}(\text{NC})_2$ . The equations representing the reactions are discussed in detail under the complex cyanides of gold (p. 390). Oxygen is essential, for the reaction.

To recover the precious metals the cyanide solution is passed through boxes containing zinc dust or turnings. Zinc dissolves while the gold and silver are precipitated;



Enormous quantities of gold have been extracted by the cyanide process from the low-grade ores of South Africa and this has been an important factor in cheapening gold, and hence raising the price of other things, and thus has contributed to the "high cost of living."

The gold production for the United States in 1915 was \$98,891,100 which is a little more than one-fifth of the world's production.

**Physical Properties.**—Gold has a high luster and a beautiful yellow color. It melts at  $1,062^\circ$  and has a density of 19.4. It is exceedingly malleable and ductile and may be beaten out into leaves  $\frac{1}{280,000}$  of an inch in thickness. Very finely divided gold usually has a purple color, although red, blue and green colloidal solutions of the metal have been obtained. Ruby glass owes its color to finely divided gold, as does "purple of Cassius" which appears to be minute particles of gold intimately mixed with stannic oxide.

Gold is a very good conductor of heat and electricity being exceeded by only silver and copper.

**Chemical Properties.**—Gold is even more resistant to chemical action than silver. It is not altered by oxygen at ordinary temperatures nor by hydrogen sulfide. It is not dissolved by any dilute acid nor by concentrated nitric or sulfuric acids, indicating that it requires a very strong oxidizing agent to cause the gold to pass into the ionic state. This is confirmed by the fact that it is dissolved by selenic acid which is a most active oxidizing agent. The metal is also dissolved by “aqua regia” a mixture of nitric and hydrochloric acids.

This mixture evolves chlorine and the gold is transformed by it into chlorauric acid,  $\text{HAuCl}_4$ , which gives the complex ion,  $\text{AuCl}_4^-$ . The chlorine, of course, cannot be a stronger oxidizing agent than the nitric acid which set it free, but it has the advantage in this case that the product of the reaction is very stable. Gold is also attacked by the fused hydroxides and nitrates of the alkali metals forming aurates. The soluble chlorine compounds of gold are easily reduced by even such feeble reducing agents as the ferrous salts or oxalic acid.

Because of its chemical resistivity, its beauty and its comparative rarity, gold has long been used for ornaments and for coinage. For such purposes, the pure metal is too soft and it is alloyed with copper or silver, usually the former. The gold coins of most countries contain 90 per cent. of gold or are 900 “fine”; those of England, however, contain 91.667 per cent. or are 916.67 fine. The composition of gold alloys is often expressed in carats, pure gold being 24 carat and 18 carat gold being  $1\frac{3}{4}$  gold.

**The Oxides and Hydroxides.**—Auric hydroxide  $\text{Au}(\text{OH})_3$ , is formed when sodium hydroxide is added to an auric solution. It acts both as a weak base and as a weak acid. When the hydroxide is carefully heated, it goes over into auric oxide,  $\text{Au}_2\text{O}_3$ , which at higher temperatures decomposes into the elements.

Aurous hydroxide,  $\text{AuOH}$ , is formed by the action of dilute potassium hydroxide upon aurous chloride. When heated to  $200^\circ$  it is changed into the oxide,  $\text{Au}_2\text{O}$ , and this decomposes at  $250^\circ$ .

**The Halogen Compounds of Gold.**—Gold will combine directly with chlorine or bromine to form auric chloride or bromide,  $\text{AuCl}_3$ ,  $\text{AuBr}_3$ . These compounds combine with hydrochloric

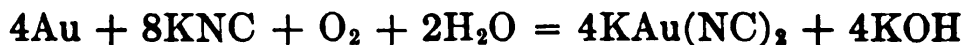
hydrobromic acid or with the corresponding halide salts, forming chlorauric or bromauric acids or their salts. The sodium chloraurate,  $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$ , is a common commercial salt and is used in photography as noted above in the toning of silver prints. Chlorauric acid is formed by dissolving gold in aqua regia.

When either the simple chloride or bromide or the complex acids are cautiously heated, aurous chloride or bromide is formed. At still higher temperatures, these decompose into the free halogen and the metal. They are not soluble in water, but slowly decompose in contact with it forming the auric compound and free gold. This is much like the behavior of some of the cuprous compounds. Auric iodide is decidedly unstable and passes easily into the aurous compound even at ordinary temperatures.

**Sulfides.**—Hydrogen sulfide precipitates a mixture of aurous sulfide,  $\text{Au}_2\text{S}$ , and auric sulfide,  $\text{Au}_2\text{S}_3$ , from auric solutions. These sulfides are soluble in the alkaline sulfides owing to the formation of the thioaurites,  $\text{K}_2\text{AuS}_2$ , and thioaurates,  $\text{KAuS}_2$ . In this respect gold is like antimony, arsenic, and tin.

**The Complex Cyanides.**—One of the most important chemical properties of gold is its ability to form complex ions with cyanogen; aurocyanogen,  $\text{Au}(\text{NC})_2^-$ , and auricyanogen,  $\text{Au}(\text{NC})_4^-$ , are well-known examples of such ions. They are formed by the action of an excess of sodium or potassium cyanide upon the compounds of gold. They are very stable and the solutions are utilized in gold electroplating, an anode of gold being used and the object to be plated being made the cathode.

The aurocyanides are of especial importance, because it is through their formation that a large part of the gold is extracted from its ores. This depends upon the fact that finely divided gold is dissolved by solutions of potassium or sodium cyanides when in contact with the air. The equation for the reaction is as follows:



The reaction is really ionic so that it succeeds as well with the cheaper sodium cyanide as with the more expensive potassium salt.

**Analytical Properties of Gold.**—Gold may be detected by its reduction to the metallic state by ferrous salts, oxalic acid, or stannous chloride. It is almost invariably determined by the fire assaying processes. This is often done as follows: a weighed quantity of the material containing gold is mixed with a relatively large quantity of lead and a little borax and heated in a shallow clay dish called a scorifier (Fig. 64) to a fairly high temperature in contact with the air. A part of the lead and practically all of the copper and other impurities in the gold save the silver are

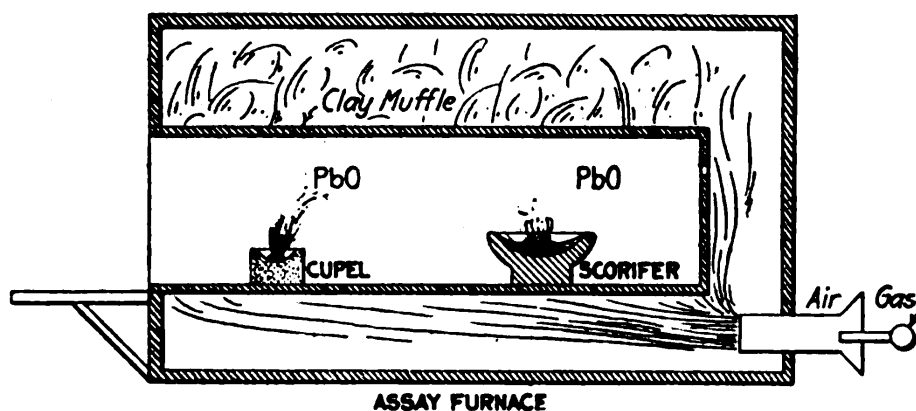


FIG. 64.

oxidized, and these together with the "gangue" form a sort of a glass with the borax and the lead oxide which is formed. At the close of this operation the molten mass is poured into a mold and allowed to cool. A lead button containing the gold and silver is obtained. This is then heated to a high temperature in contact with the air in a "cupel" or little cup made of bone ash, the lead oxidizes and the oxide is absorbed in the cupel. There is finally left a button of gold and silver. The silver is then removed by treating the alloy with nitric acid which does not dissolve the gold. The fire assay is a smelting process carried out on a small scale.

## CHAPTER XXV

### GROUP III



The elements of this group fall naturally into two sub-groups, the rare earth metals and the aluminum sub-group. The members of the first are scandium, yttrium, and lanthanum, those of the aluminum sub-group are boron, aluminum, gallium, indium, and thallium. The elements are all trivalent although some have other valencies in addition. As was the case in groups I and II the members which stand in the left hand column of the group as it appears in the periodic system, scandium, yttrium, and lanthanum are stronger bases than those of the aluminum group which are on the right. Aluminum is the third element in the order of abundance in the earth's crust, boron is fairly abundant and all the other members of the group are decidedly rare.

**The Rare Earth Metals.**—The metals of the rare earths are found in a large number of rare minerals each of which contains a great many elements. The names of a few of these minerals are euxenite, gadolinite, orthite, and monazite. Monazite is found in considerable quantities in North and South Carolina, but comes chiefly from Brazil. The hydroxides of the members of this sub-group are fairly strong bases and are not soluble in excess of sodium or potassium hydroxides.

#### SCANDIUM

Scandium whose atomic weight is 44.1 is interesting because it is one of the elements whose existence and properties were predicted by Mendelejeff. See p. 272. Its hydroxide  $\text{Sc}(\text{OH})_3$  is a colorless gelatinous precipitate soluble in acids but not in bases. The salts are colorless and are not especially

hydrolyzed. The salts of the oxy-acids as well as of the halogen acids are known.

#### YTTRIUM

Yttrium has an atomic weight of 89. The metal decomposes water slowly, its hydroxide is colorless and gives colorless salts. It is a stronger base than scandium hydroxide.

#### LANTHANUM

Lanthanum, La, atomic weight 139, is an iron-gray colored metal, which is very slowly acted upon by water. It dissolves in dilute acids. The hydroxide is white and somewhat soluble in water, the solution is alkaline, absorbs carbon dioxide and decomposes ammonium salts. It is the strongest base of the group.

There are several elements, some of them of rather doubtful individuality, whose atomic weights are near to that of lanthanum and which so far as that is concerned have a claim on the same position in the periodic system. They have so nearly the same properties that it is difficult to separate them. Ostwald has likened this group of closely related elements with about the same atomic weight which appear in the periodic system where one element might be expected, to the planetoids which are found in the solar system where one large planet might be looked for.

**The Aluminum Sub-group.**—The first member of Group III and of this sub-group is boron, atomic weight 11. This is almost exclusively an acid-forming element; that is to say, it does not form cations, and for that reason has already been treated among the non-metals.

#### ALUMINUM

**General.**—Aluminum is the most abundant of the metals. It is trivalent, and is like zinc in that its hydroxide is soluble both in acids and in bases. In addition to its fairly close relationship to the other members of this sub-group, it is very much like ferric iron and trivalent chromium as will be seen when these metals are studied.

**Occurrence.**—Aluminum is never found free but its compounds are exceedingly abundant, since it is an essential constituent of nearly all rocks except the sand-stones and limestones and is almost invariably present in these. It is found as the double silicates, the feldspars and the micas; as the simple silicate clay; as the double fluoride with sodium in cryolite; as the oxide corundum; as the hydroxide and the partially dehydrated hydroxide in bauxite; and in many other compounds. The ruby is aluminum oxide colored by a little chromium, the garnet is calcium aluminum silicate, and turquoise is a basic phosphate.

**Preparation of the Metal.**—Metallic aluminum is prepared by the electrolysis of highly purified aluminum oxide dissolved in a

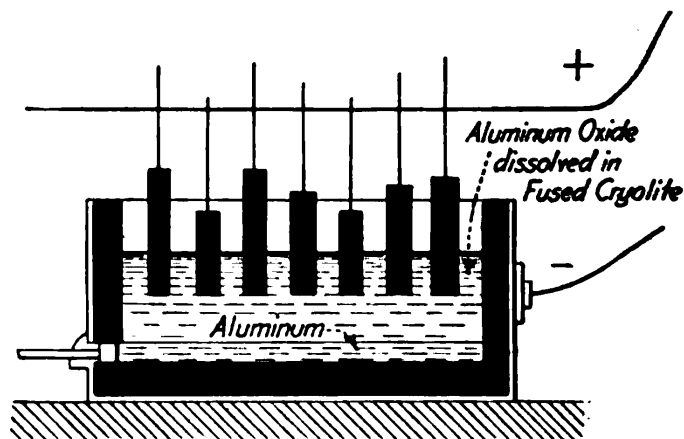


FIG. 65.

molten bath the basis of which is cryolite,  $\text{Na}_3\text{AlF}_6$ . The electrolysis is carried out in iron cells (Fig. 65) lined with carbon which is made the cathode, the anodes being large carbon rods. The current is high, about 10,000 amp. per cell, while the drop of potential around the cell is about 5 volts. The bath is kept melted by the heat produced by the current in overcoming the resistance. Upon electrolysis after the addition of the oxide, the metal collects at the cathode and runs down to the bottom of the cell while oxygen is evolved, and combines largely with the carbon anodes. As the process goes on more aluminum oxide is added from time to time, and the metal is tapped off so that the operation is continuous. This process differs materially from most metallurgical operations in that it is impracticable to purify the product, and so it is necessary to start with the very purest

raw material. The aluminum oxide is made from bauxite, and the simplest process for its purification is to melt the bauxite in an electric furnace with the proper amount of carbon. This reduces the oxides of iron, silicon, and titanium which are present and leaves the aluminum oxide untouched. The metallic aluminum is very pure, often running 99.9 per cent.

**Physical Properties.**—Aluminum is a white metal with a bluish cast. It melts at  $658^{\circ}$  and has a density of 2.7 becoming 2.72 if it is hammered or rolled. The cast aluminum is about as hard as pure silver while the hammered is as hard as soft iron. Its tensile strength is high although much lower than that of steel. It is malleable and ductile and may be rolled or hammered into very thin sheets or drawn into fine wire. It is best worked at 100 to  $150^{\circ}$ . At temperatures near its melting-point it becomes so brittle that it may be easily powdered in a mortar. It is not readily worked in a lathe, but many of its alloys are.

Alloys with magnesium known as magnalium are very light, easily machined and fairly strong. Aluminum bronze has already been discussed under copper.

Pure aluminum has a high conductivity for electricity, about two-thirds that of copper for conductors of equal cross-section, but since the density of aluminum is so much smaller than that of copper, an aluminum conductor will weigh less than a copper conductor of equal carrying capacity.

**Chemical Properties.**—Metallic aluminum is really a very active element and passes into its compounds with a great decrease in free energy, and yet it acts in the main like a rather inert metal. It seems not to be acted upon by air or water or many other chemical agencies. But this indifference is apparent rather than real and is due to the formation of a very thin, closely adhering film of the oxide which acts as a sort of varnish, and in a great measure protects the metal from further attack. Aluminum may be amalgamated by contact with solutions of mercuric chloride. The aluminum oxide seems to be unable to cling to the surface of the fluid or semi-fluid aluminum amalgam, and the latter shows the real activity of the metal. It is rapidly acted upon by air and water giving hydrogen and aluminum hydroxide.

Aluminum dissolves in solutions of sodium hydroxide with the

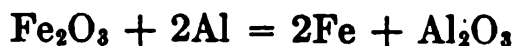
evolution of hydrogen. The explanation for this action is found in the fact that sodium hydroxide will dissolve aluminum oxide, and therefore it is supposed that it removes the protecting film from the surface of the metal and allows the latter to display its activity. Because of this protecting film, massive aluminum is but superficially attacked even at high temperatures by the air. The powdered metal, however, will burn with a very bright light when blown into a flame especially if carried by a stream of oxygen. It is sometimes used in flashlight powders. Aluminum dissolves readily in hydrochloric acid, not so easily in dilute sulfuric, and very slowly in dilute nitric. In the two former cases, hydrogen is evolved while in the latter, ammonium salts are produced. The difference in the rate of attack is probably connected with the film mentioned above. Another phenomenon which is probably due to this is, that if a piece of aluminum is made anode in certain salt solutions, sodium sulfate, carbonate, phosphate, etc., it will not allow a current to pass until a certain potential is reached, which in the case of the phosphate is 300–400 volts; while if it is made the cathode, the current passes easily at a low voltage. The aluminum electrode changes its properties very rapidly with the change in the direction of the current, and this property may be made the basis of a method for changing an alternating into a direct current. It is also of use in certain kinds of lightning arrestors.

Aluminum is trivalent in all of its compounds. Its hydroxide acts both as an acid and as a base and therefore cannot be strong in either way, consequently both classes of salts are hydrolyzed to a certain degree.

The atomic weight of aluminum is 27.1.

**Goldschmidt Process.**—The most striking chemical property of aluminum is its great tendency to combine with oxygen. As mentioned above this is generally concealed by the film of oxide, but under the proper conditions, aluminum will reduce all other oxides except magnesium. To bring this about, the oxide to be reduced is mixed in the proper proportions with powdered aluminum (Fig. 66) and the mixture heated at one point to a high temperature by burning magnesium or a mixture of magnesium and potassium chlorate, when a very vigorous reaction takes place which spreads through the entire mixture. The

temperature attained is usually high enough to melt the other metal and the aluminum oxide. Naturally it varies with the oxide reduced. The process was invented by Goldschmidt and called by him "Aluminothermy" and the mixtures "thermite." They are used both to get high temperatures and pure metals. The equation for the reaction with ferric oxide is,



This reaction produces a temperature of  $3,000^\circ$  and is often used for welding operations and in the repair of breaks in large castings or forgings. It can be used almost anywhere and has proved to be of very great benefit for making repairs at a distance from a machine shop. With sulfides, a very similar reaction takes place, aluminum sulfide,  $\text{Al}_2\text{S}_3$ , and the metal being formed.

**Aluminum Oxide and Hydroxide.**—Aluminum oxide,  $\text{Al}_2\text{O}_3$ , or alumina as it is often called, is found in nature in the mineral corundum. When colored red by chromium it is called ruby, when blue, sapphire. Corundum mixed with magnetite is called emery. Corundum is next to diamond and carborundum

(silicon carbide) in hardness, and is used for making wheels for grinding. Aluminum oxide which has been fused in an electric furnace is identical with corundum and is now being used instead of the mineral under the name "alundum." Artificial rubies which are identical with the natural stones, are made by fusing a mixture of aluminum oxide and a chromium compound.

Aluminum hydroxide is found in nature in the mineral hydrargillite,  $\text{Al}(\text{OH})_3$ , and may be made in the laboratory by the addition of a solution of a base or of a carbonate to a solution of an aluminum salt. It is not soluble in water, but is dissolved by acids and by strong bases, resembling the hydroxides of beryllium and zinc in this respect. It differs from zinc hydroxide in that

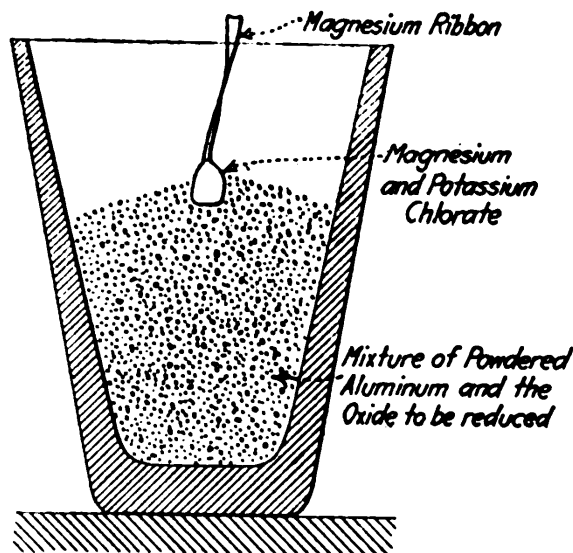


FIG. 66.

it is very slightly soluble in ammonium hydroxide. The hydroxide dissolves in acids because of the usual dissociation of the bases into the cation and hydroxyl the concentration of the latter being decreased by the hydrogen. The bases dissolve it, because it splits off the hydrogen ion and forms the aluminate ion  $\text{AlO}_2^-$ ,



The hydroxyl ion of the base unites with the hydrogen ion and decreases its concentration. The salts formed are aluminates. Sodium aluminate and the corresponding potassium salt,  $\text{NaAlO}_2$  and  $\text{KAlO}_2$ , are soluble in water, but are highly hydrolyzed because aluminum hydroxide is a very weak acid. Most of the aluminates are insoluble and many are found in nature; those of the bivalent metals are called spinels from the magnesium aluminate, spinel,  $\text{Mg}(\text{AlO}_2)_2$ , which is the typical mineral of the class.

Because of the great weakness of aluminum hydroxide as a base, aluminum carbonate does not exist, and aluminum hydroxide is precipitated upon the addition of carbonates to solution of aluminum salts. Obviously salts of other weak acids will work in the same way and  $\text{Al}(\text{OH})_3$  is precipitated by solutions of alkali sulfides and cyanides.

**Aluminum Chloride.**—Aluminum chloride,  $\text{AlCl}_3$ , is the most important of the artificially prepared halogen compounds of aluminum. It may be obtained in the form of a crystalline hydrate,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , from solutions prepared by dissolving the hydroxide or metal in hydrochloric acid. When heated to drive off the water, the chloride is completely decomposed, aluminum oxide and hydrochloric acid being formed. The anhydrous chloride may be obtained by heating the metal in chlorine or in hydrogen chloride. It is a white crystalline solid which sublimates without melting and fumes when exposed to moist air. The anhydrous salt is used in organic chemistry as a catalytic agent.

Because aluminum hydroxide is a weak base the solutions of aluminum salts, including the chloride, are acid in reaction from hydrolysis, and generally can be kept clear only in the presence of an excess of acid.

**Aluminum Sulfate.**—Aluminum sulfate,  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , is made on a large scale from sulfuric acid and either aluminum

hydroxide or aluminum silicate,  $\text{H}_2\text{Al}_2(\text{SiO}_4)_2 \cdot \text{H}_2\text{O}$  or kaolin as it is often called. At the present time, the hydroxide is more commonly used. It is very soluble in water and the solution is acid because of hydrolysis. Its trade name is "concentrated alum." It is used as a mordant in dyeing, in sizing paper to prevent the spreading of ink, and in clarifying water. When a solution of potassium sulfate is added to a strong solution of aluminum sulfate, octahedral crystals of a double salt named alum,  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , are formed. This is the type of a rather large number of double salts which are isomorphous and are called alums. To distinguish it from the others, it is usually called potassium alum. The alums have the general formula  $\text{M}^+ \text{M}^{+++} (\text{AO}_4)_2 \cdot 12\text{H}_2\text{O}$  in which  $\text{M}^+$  represents any member of the alkali metals except lithium and in addition ammonium, silver, and monovalent thallium;  $\text{M}^{+++}$  stands for aluminum, gallium, indium, trivalent iron, chromium, and manganese; and finally A may be either sulfur or selenium. The aluminum alums are distinguished by prefixing the name of the monovalent metal while in the case of the other alums both the mono- and trivalent metals are named, for example, potassium chrome alum,  $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ . The  $12\text{H}_2\text{O}$  is an essential part of an alum. Double sulfates are known which differ from alums only in this respect and yet they are not alums. Since the alums are isomorphous they can all form mixed crystals and a single crystal may contain a large number of elements.

Potassium alum is the most important alum; it was formerly the most important aluminum salt but has now been largely replaced by the sulfate. It may be prepared by roasting alunite, a basic alum found in Italy, Hungary, and in southwestern United States and extracting with hot water. The crystals melt or dissolve in their own water at  $92^\circ$ .

Solutions of alum are acid and will react with carbonates and bicarbonates with the evolution of carbon dioxide, the precipitation of aluminum hydroxide and the formation of a solution of the sulfates of potassium and the metal of the carbonate. It is upon this property that its use in cheap baking powders depends. The soluble sulfates formed impart a strong bitter taste to the food and the use of such powders is objectionable on this account, if for no other. A solution of alum will dissolve a considerable

quantity of aluminum hydroxide forming the so-called "neutral alum,"  $\text{KAl}_2(\text{OH})_3(\text{SO}_4)_2$ . It is used as a mordant in dyeing and as a clarifying agent in the purification of water. The aluminum hydroxide which it readily forms is the active agent in each case. In the clarification of water the precipitated aluminum hydroxide attaches itself to the silt suspended in the water and also to most of the bacteria present and carries the whole to the bottom.

Alum loses all of its water at  $100^\circ$ . It is then known as burnt alum, and is used in medicine.

**Mordants.**—Some dyes will combine directly or enter into solid solutions with the fiber of the cloth while others may be precipitated as insoluble substances within the fiber, but many others do not have either of these characteristics. Such dyes require a mordant, *i.e.*, a substance which will attach itself firmly both to the fiber and to the dye. Aluminum hydroxide is such a substance. The cloth to be dyed is first treated with a solution of an aluminum salt in such a condition that it contains a considerable amount of aluminum hydroxide; neutral alum, aluminum sulfate, acetate, or sodium aluminate serve well; and it is then boiled with the dye. Dyes more often require mordants with cotton than with wool or silk. Aluminum hydroxide, even in the absence of the fiber, will take up many dyes forming what are known as "lakes."

**Aluminum Acetate.**—Aluminum acetate,  $\text{Al}(\text{C}_2\text{H}_3\text{O}_2)_3$ , may be made by the action of the sulfate in solution upon lead or barium acetate, lead or barium sulfate being precipitated. Since it is a salt of a weak acid and of a weak base it is strongly hydrolyzed, and on this account is used in mordanting cloth and also in making it waterproof. The same result may be secured at a lower cost by using aluminum sulfate and sodium acetate.

**Aluminum Sulfide.**—Aluminum sulfide,  $\text{Al}_2\text{S}_3$ , cannot be prepared in a wet way. It is formed by the action of finely divided aluminum on sulfides at a high temperature by practically the methods of the Goldschmidt process.

**Aluminum Silicate—Clay.**—The rocks which originally composed the earth's crust were very largely complex silicates and almost invariably contain aluminum as one of their constitu-

**nts.** By the action of the carbon dioxide of the air and of water, these rocks gradually decompose or weather as it is called, and aluminum silicate is one of the products. The aluminum silicate being practically insoluble and in an extremely fine state of division is carried by flowing water and deposited when the latter reaches a quiet lake or the ocean, forming the beds of clay. These evidently have a very good chance to become contaminated and are rarely pure. The purest clay, kaolin or china clay,  $\text{H}_2\text{Al}_2(\text{SiO}_4)_2 \cdot \text{H}_2\text{O}$ , has probably been formed by the decomposition of feldspar,  $\text{KAlSi}_3\text{O}_8$ , the potassium carbonate being carried away and the kaolin left where it was formed. Common clay contains some calcium carbonate, iron oxide, quartz, etc. When comparatively pure it is known as potters earth. Marl contains large quantities of calcium carbonate. Ocher, umber and sienna are clays colored by oxides of iron and manganese. They are used to some extent as pigments.

Clay, as is well known, becomes plastic when moist and may be easily worked into almost any shape desired. When dried and then heated to a high temperature it shrinks, becomes quite hard, and loses its power of becoming plastic with water. It also becomes resistant to chemical change and acquires considerable mechanical strength. Because of these properties it is used for making brick, pottery, and porcelain. The chemical change which takes place during the heating consists in the driving off of all of the hydrogen and part of the oxygen in the form of water. Pure kaolin cannot be melted in the furnaces for firing this material, but the presence of compounds of the alkalies, calcium or magnesium carbonates or especially of oxide of iron causes the mixture to fuse partially and become more or less pasty while in the furnace, and stronger after the firing. The iron imparts the red color commonly associated with brick. Fire brick is made from nearly pure clay and has a high melting-point to which it owes its name. Articles made from clay are more or less porous after firing, and for many purposes they must be glazed. This is accomplished in various ways as will develop.

**Porcelain and Pottery.**—Porcelain is the name applied to the highest grade of ware made from clay. It is made by grinding together very pure kaolin and feldspar in the proper proportions, and making up into a plastic mass from which the desired articles

are formed. After drying, these are fired at such a temperature that the feldspar melts and binds the burned kaolin together into a hard translucent mass which is nearly homogeneous but does not have a glaze. To secure the latter the articles are dipped into a suspension of very finely ground feldspar in water, the ware becomes coated with a thin layer of the feldspar, and after drying is fired once more at a high temperature and is then allowed to cool slowly (annealed). The ware is then translucent and has a smooth glaze which is practically a glass. It is very difficultly fusible and decidedly resistant to chemical action, but is attacked by aqueous and fused alkalis.

Semiporcelain is made from a white plastic clay to which is added ground quartz, flint, or feldspar. After the first burning it is porous and is glazed with a mixture of borax, quartz, sodium carbonate, and oxide of lead. The ware is usually much thicker than porcelain and is not very suitable for chemical purposes.

Earthen-ware is made from colored plastic clay, the impurities of which serve to frit or bind the kaolin together. It is glazed by throwing common salt into the kiln toward the close of the burning. At the high temperature, the salt volatilizes and reacts with the clay and the water vapor present so as to form an easily fusible silicate which fills the pores of the ware. Unglazed earthenware is largely used in the form of tile, bricks, flower pots, etc.

**Ultramarine.**—A double silicate of sodium and aluminum containing some sulfur is found in nature as the mineral lapis lazuli which has approximately the composition  $(\text{NaAlSiO}_4)_x \cdot \text{Na}_2\text{S}_2$ . It has a very beautiful blue color and is used for ornamental purposes. When ground it forms the pigment known as ultramarine. This same pigment may be made very cheaply by heating together sodium sulfate, carbon, and clay. The resulting blue compound is ground and washed with water. Since it is very cheap and is stable toward light, air and alkalis it is much used as a pigment in water color paints, wall paper, laundry blue, etc. It was formerly used to disguise the faint yellow color of granulated sugar. It loses its color on contact with even very weak acids and the loss of color is accompanied by the evolution of hydrogen sulfide. The blue color of the compound is something of a puzzle because its components might

naturally be expected to yield a colorless substance. By varying the methods of manufacture, green, violet, and red varieties may be obtained.

**Hydraulic Mortars and Cements.**—When a limestone containing something like 8 to 18 per cent. of clay is “burned” in the ordinary way the product will slake and form a mortar which will set and harden under water and hence is called hydraulic cement. A much better product is made by burning a limestone which contains 20 per cent. or more of clay until the carbon dioxide is driven off. The substance so produced will not slake; but if finely ground and mixed with water, will set and harden out of contact with the air. This is known as **natural cement**.

**Portland cement** is the best hydraulic cement. *It is the finely pulverized product made by heating to incipient fusion a properly proportioned mixture of silica, aluminum silicate, and calcium carbonate to which an addition of not more than 3 per cent. of gypsum has been made after the heating.* The essential constituents of Portland cement are lime, silica, and alumina. Under commercial conditions some of the alumina is always replaced by ferric oxide, and a little of the lime by magnesia.

Portland cement may be made from almost any materials which give the proper mixture of calcium carbonate, silica, and aluminum silicate provided they do not contain more than 4 per cent. of magnesium carbonate and that the silica is in a very fine state of subdivision. The most widely used materials for the preparation of this cement are limestone and clay or shale; these are very finely ground and thoroughly mixed in such proportions that the mixture shall contain close to 75 per cent. of calcium carbonate and 20 per cent. silica, alumina and ferric oxide taken together, the remaining 5 per cent. being magnesium carbonate, alkalies, etc. Some limestones have approximately this composition, and are called “cement rock” since they require merely the addition of a little of a purer limestone or of a suitable clay to correct their composition.

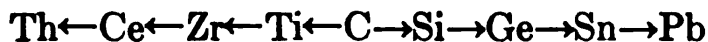
After the components of the cement have been ground very fine and thoroughly mixed in the proper proportions, they are then fed into the upper end of a long, slightly inclined rotary kiln through which they gradually work their way against the flames and hot gases of a fire of powdered coal which is blown into the

metal dissolves readily in dilute and concentrated sulfuric acids and less readily in hydrochloric. Thallium forms two series of compounds. In one, the thallic series, it is trivalent and resembles aluminum to a certain degree, but the hydroxide is not soluble in bases and the sulfate does not form alums.

In the other the monovalent or thallic series it presents a curious set of relationships. The hydroxide,  $\text{TlOH}$ , is soluble in water and is a strong base. The carbonate, phosphate, sulfate and oxalate are soluble. These properties are very remarkable for a heavy metal, and are like those of an alkali metal. This resemblance is further strengthened by the facts that the sulfate forms the compound  $\text{Tl}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ , isomorphous with the corresponding potassium salt, and also forms alums with the ferric, chromic, or aluminum sulfates, which are isomorphous with ordinary alum. The fluoride is easily soluble while the rest of the halides are but slightly soluble, the solubility decreasing from the chloride to the iodide. The chloride changes from white to violet in the light. The chromate is slightly soluble. In all these ways it is like silver. It resembles lead in that the chloride is not dissolved by ammonia but is by hot water.

## CHAPTER XXVI

### GROUP IV



The members of Group IV, like those of the preceding groups, divide themselves into two sub-groups, which may be named the titanium and the germanium sub-groups. There is not as marked a difference in the properties of the two as was the case with the preceding groups, and yet the same general relationship holds here. The basic character of the elements increases with the atomic weight. The members of the titanium groups, which occupy the left-hand column in the table as it is arranged, are, on the whole, stronger bases than those on the right-hand side, the germanium group. This, it will be recalled, has been the case in each of the preceding groups of metals. The gradual weakening in the basic properties, which has been noticeable in passing to each successive group, is continued with this and there is no really strong base formed by a member of the group, in fact, the first two members, carbon and silicon, are distinctly non-metallic, and have been discussed among such elements. The maximum valence of the members of the group is four.

#### TITANIUM SUB-GROUP

The members of this sub-group are titanium, atomic weight, 48.1; zirconium, atomic weight, 90.6; cerium, atomic weight, 140.25; and thorium, atomic weight, 232.4.

#### TITANIUM

Titanium is a widely distributed and comparatively abundant element being present in almost all igneous rocks and forming a larger per cent. of the lithosphere than carbon. It does not occur free in nature, and its compounds are not collected in great

beds like the coal beds, so it is not as available as carbon. It occurs in a number of minerals, such as rutile,  $\text{TiO}_2$ , and titanite,  $\text{FeTiO}_3$ . The metal dissolves in acids with the evolution of hydrogen, and decomposes steam at a high temperature. It forms three series of compounds in which it is di-, tri-, and tetravalent; the last are the most stable. Titanic hydroxide is rather more of an acid than of a base but acts in both ways. Metallic titanium has a great tendency to combine with nitrogen, oxygen and sulfur. An alloy of metallic titanium with iron, called ferrotitanium, is often used in the manufacture of steel. The titanium increases the tensile strength and toughens the steel. The carbide is used in special kinds of flaming arc lamps, burning titanium carbide as cathode below a copper anode.

#### ZIRCONIUM

**Zirconium** is a rare metal, which is found chiefly as zircon, the silicate  $\text{ZrSiO}_4$ . Its hydroxide is a weaker acid and a stronger base than titanium hydroxide.

#### CERIUM

**Cerium** is a rare metal which is chiefly found in cerite, a hydrated silicate, which contains calcium, cerium, and lanthanum, and the other rare earths which so closely resemble lanthanum. The metal burns more readily than magnesium and the small particles thrown off, when it is scratched with a hard object, take fire. For this reason an alloy of cerium and iron which gives brilliant sparks when rubbed with a file is used as a gas lighter. Cerium dioxide is used in connection with thorium dioxide in the preparation of incandescent mantles, as will soon be described. Cerium forms two series of compounds, in one it is trivalent and strongly resembles the rare earths, while in the other it is tetravalent, and is like the other titanium metals.

#### THORIUM

**Thorium** is obtained chiefly from monazite, a phosphate of cerium and thorium. Thorium hydroxide is the strongest base

of the titanium series. The nitrate,  $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$  is the most important salt. It is used in the formation of Welsbach incandescent gas mantles. These are made by dipping a mantle woven from ramie fiber into a solution of thorium nitrate along with about 1 per cent. of cerium nitrate,  $\text{Ce}(\text{NO}_3)_4$ . After drying, the ramie is burned away, and the nitrates are converted into the oxides which retain the form of the mantle. A mixture of the two oxides in the proportions given is very efficient as a light producer, while pure thorium dioxide, or a mixture containing more cerium, is not nearly so good.

Thorium and its compounds are radioactive, but nowhere near as highly so as the radium compounds. A discussion of this phase of the properties of thorium will be postponed until later, when all the radioactive elements may be treated together.

#### GERMANIUM SUB-GROUP

The members of this sub-group are both di- and tetravalent. In their divalent compounds, they are more strongly basic than in the other series.

#### GERMANIUM

Germanium, atomic weight, 72.5, is a rare element. Its properties agree closely with those predicted by Mendelejeff for eka-silicon, germanium being then undiscovered. The element itself is distinctly metallic, but its compounds are much more like those of the non-metals than the metals. It bears a strong resemblance to carbon and silicon, as may be seen from the formulas of a few of its compounds,  $\text{GeH}_4$ ,  $\text{GeF}_4$ ,  $\text{GeCl}_4$ ,  $\text{GeCl}_2$ ,  $\text{GeHCl}_3$  (germanium chloroform),  $\text{GeO}_2$ ,  $\text{GeO}$ ,  $\text{GeS}_2$ ,  $\text{GeS}$ . The dioxide has acid properties, but also dissolves in acids. The sulfide, like zinc sulfide, is white.

#### TIN

The discovery of tin is prehistoric, the metal having been used by early man in making his bronze tools and weapons.

**Occurrence and Metallurgy.**—The chief ore is tin stone, or cassiterite,  $\text{SnO}_2$ . This is found in many places, but chiefly in the East Indies, Bolivia and Cornwall. It is easily reduced to

the metallic state by carbon, the greatest difficulty in the metallurgy of tin being the purification of the oxide before its reduction. This is done by crushing the ore and mechanically separating the granite or other rocky gangue. The concentrated ore is then repeatedly roasted and washed to remove the sulfides of arsenic, iron and copper. The purified stannic oxide is then reduced in reverberatory furnaces with carbon in the form of anthracite coal. The tin so obtained contains some iron and arsenic. These combine with a little tin to form a compound having a higher melting-point than the pure tin, so that the latter may be purified by carefully heating the ingots to a very little above the melting-point of tin, and allowing the purer metal to run away from the iron arsenic alloy. This process is called liquation. The purest tin is that from Banca. The world's production of tin in 1914 was 120,400 tons.

**Physical Properties.**—Tin is a silvery white highly lustrous crystalline metal, which exists in several enantiotropic modifications. The one which is the most familiar is stable from  $18^{\circ}$  to  $161^{\circ}$  and is known as tetragonal, or ordinary tin. Below  $18^{\circ}$  it becomes meta-stable, and may pass over into a gray powdery modification, with a considerable increase in volume, since the density of the gray tin is 5.8, while that of the ordinary tin is 7.3. This is, of course, accompanied by the injury or destruction of any object made of the tin. The change is known as the "tin disease" and has caused the gradual decay of organ pipes, etc., in the northern part of Europe where the temperature averages lower than  $18^{\circ}$ . This change is most rapid at  $-50^{\circ}$ . The transformation is very easily suspended and in the absence of the gray modification, ordinary tin will remain at temperatures somewhat below  $18^{\circ}$ , practically indefinitely. At  $161^{\circ}$ , tetragonal or ordinary tin changes into rhombic, which is stable up to the melting-point,  $232^{\circ}$ . Tin is very malleable and may be beaten or rolled into thin sheets, known as tin foil. Cast tin is crystalline and when bent gives out a peculiar sound known as the "cry of tin." Tin plate or "tin," as it is generally called, is made by dipping carefully cleaned sheets of mild steel into molten tin. The tin forms an alloy with the iron and this, in turn, becomes covered with a thin layer of practically pure tin. Such plate owes its usefulness to the fact that metallic tin is

unaffected by air, water, or by weak acids in the absence of air. As is well known, very large quantities of tin plate are used in making cans and utensils. The greater part of these soon find their way to the rubbish heap and the tin is lost. This waste is regrettable because the supply of tin ore seems to be limited. Attempts are being made with somewhat encouraging success to recover the metal from such waste plate. One very serious drawback is the cost of collection.

There are in use two important methods for the recovery of tin. In one the tin plate is made anode in a solution of sodium hydroxide. The tin dissolves as sodium stannate and is deposited on the cathode. In the other, the plate is exposed to the action of chlorine which attacks the tin much more easily than the iron. Each of these methods works well on the clean scrap left in the manufacture of tinned articles and about one-fourth of the tin used in this country is recovered in these ways.

A piece of tin plate which has once got a hole scratched through the tin down to the iron will rust more rapidly at that place than a piece of pure iron. This is due to the fact that in the presence of water an electric battery is formed with the iron acting like the zinc in an ordinary cell, with the result that it is rapidly corroded.

Tin is a component of many alloys; bronze has been given; soft solder contains 50 per cent. each of lead and tin; pewter, 25 per cent. lead; Britannia metal 10 per cent. antimony and some copper. Tin amalgam was formerly used to back mirrors.

**Chemical Properties.**—Tin forms two series of compounds, the stannous, in which it is divalent, and the stannic, in which it is tetravalent. Stannous hydroxide is more basic than stannic and its salts are less hydrolyzed in water solutions than the stannic salts, but each hydroxide is soluble both in bases and in acids and therefore each is a weak base. Neither is a strong enough base to form a carbonate. The stannous salts are good reducing agents, passing readily into the stannic compounds.

The metal is not altered by air or water at ordinary temperatures, but oxidizes easily at higher temperatures. It dissolves readily in hydrochloric acid with the evolution of hydrogen and the formation of stannous chloride,  $\text{SnCl}_2$ . Hot concentrated sulfuric acid forms stannous sulfate,  $\text{SnSO}_4$ , and sulfur dioxide.

calico printing and is called "preparing salt." It is also used to render cotton goods permanently fire proof. The cotton is first soaked in a solution of alpha sodium stannate, dried, and then placed in a solution of ammonium sulfate. In the presence of the cation of the weak base, ammonium hydroxide, the stannate is hydrolyzed and stannic acid precipitated in the cloth.

Beta or meta stannic acid is made by acting upon tin with concentrated nitric acid. It differs from the alpha acid in that it is entirely insoluble in nitric acid, that it swells up but does not dissolve in sulfuric acid, and when treated with hydrochloric acid forms a compound which is not soluble in hydrochloric acid, but which dissolves after the hydrochloric acid is removed and replaced by water. The solution so obtained is not like that of stannic chloride and gelatinizes when boiled. Sodium hydroxide dissolves beta stannic acid and yields a salt, sodium beta stannate,  $\text{Na}_2\text{Sn}_6\text{O}_{11}4\text{H}_2\text{O}$ ; by acidulating this solution, beta stannic acid is precipitated. When beta stannic acid is fused with sodium hydroxide, the alpha stannate is formed.

When solutions of alpha stannic acid in hydrochloric or hydrobromic acid stand for a long time, beta stannic acid is gradually precipitated.

**Stannic Chloride.**—Stannic chloride,  $\text{SnCl}_4$ , is formed by the action of chlorine upon stannous chloride or upon the metal. Use is made of this in recovering tin from scraps of the plate by the chlorine process. It is a colorless liquid, which boils at  $114^\circ$ . It fumes in contact with the air. With water a number of hydrates are formed. The pentahydrate,  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ , is much used in dyeing as a mordanting agent, under the name of "oxymuriate of tin." It combines with hydrogen chloride to form chlorstannic acid,  $\text{H}_2\text{SnCl}_6$ , several salts of which are known. The ammonium salt,  $(\text{NH}_4)_2\text{SnCl}_6$ , was formerly much used as a mordant in dyeing under the name of "pink salt," not because it had a pink color but because it was used in dyeing pinks.

Solutions of the chloride in water are very slowly hydrolyzed. The stannic hydroxide remains in solution in the colloidal state, and is gradually transformed into beta stannic acid.

**Stannic Sulfide.**—Stannic sulfide is precipitated as a yellow amorphous substance by passing hydrogen sulfide through a moderately acid solution of a stannic salt. It is soluble in con-

centrated hydrochloric acid, and is reprecipitated by diluting the solution. It is also soluble in solutions of ammonium sulfide or of the alkali sulfides, forming thiostannates,



Upon acidulation with dilute acids, thiostannic acid is formed, which at once decomposes to give stannic sulfide and hydrogen sulfide.

**Analytical Properties.**—The properties of stannous sulfide and those of stannic sulfide, which have just been given, put it in an analytical group with arsenic and antimony, which is distinguished from that containing mercury, copper, cadmium, bismuth, and lead by the fact that the sulfides of the last mentioned metals are not soluble in ammonium sulfide (copper is slightly soluble). In solution, both the stannic and stannous compounds are colorless. The stannous are distinguished from the stannic by the dark color of the sulfide and by the fact that the former are strong reducing agents.

### LEAD

**Lead** is the member of the germanium sub-group with the highest atomic weight, 207.2. Although it occurs free in nature in insignificant quantities, it is so easily smelted from its ores that it was well known to the ancients. It was used by the Romans for water pipes, a use to which it is still put.

The chemical relationships of lead are somewhat varied, as is often the case with the last member of a sub-group. It is both di- and tetravalent. In the divalent state, lead resembles barium in several ways, in others it is like silver and thallium. The hydroxide,  $\text{Pb}(\text{OH})_2$ , acts both as a base and an acid in that it dissolves and forms salts with both acids and bases. In this way lead is like zinc. The hydroxide is a stronger base than acid, so that its salts with the stronger acids are fairly stable in solution. The tetravalency of lead shows its relationship to the other members of this group, but the resemblance is not very strong. The hydroxide,  $\text{Pb}(\text{OH})_4$ , is both basic and acidic; but is a very weak base, so that its salts, even with the strongest acid, are practically completely hydrolyzed. The tetravalent lead compounds tend to pass to the divalent state and are good oxidizing

agents, so the oxidation relationships are the reverse of those between stannous and stannic tin.

**Occurrence.**—The principal ore of lead is galena, lead sulfide,  $\text{PbS}$ , which contains, when pure, 86.57 per cent. of lead. It is found in nearly all countries and very often carries silver, either as finely divided native silver, or as isomorphous sulfide, disseminated through it.

Other common ores of lead are the carbonate, cerusite,  $\text{PbCO}_3$ , and sulfate, anglesite,  $\text{PbSO}_4$ . They are formed as decomposition or oxidation products from galena, and are consequently found near the surface in mines which lower down yield galena almost exclusively.

**Metallurgy.**—Since lead sulfide is the chief lead ore, the extraction of lead from its ores is largely devoted to the treatment of this compound. This is accomplished entirely by smelting or dry processes, and the blast-furnace process is used almost exclusively.

The lead blast-furnace, Fig. 68, is rectangular in shape and is from 15 to 25 ft. high, 10 to 20 ft. long and from 3 to 5 ft. wide at the bottom. A row of blast pipes, or tuyères, along each side of the furnace, serve to introduce the air blast, which has a pressure of from 1 to 3 lb.

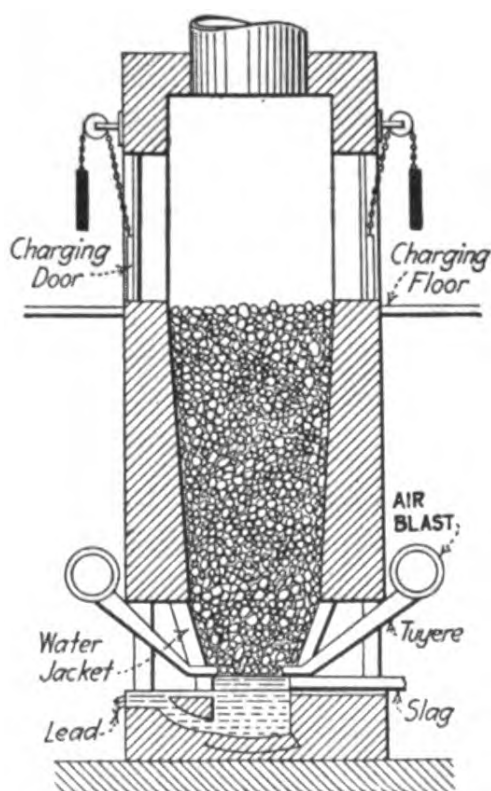
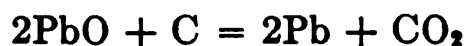


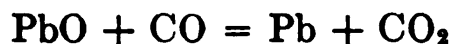
FIG. 68.

The lead ore mixed with coke to furnish heat for smelting, and sufficient limestones to flux off the silica from the gangue, is charged into the furnace. A part of the lead ore is charged raw, that is, unroasted, while another portion is previously roasted to lead oxide in a separate roasting furnace. This roasted ore usually has in it a considerable quantity of iron oxide, which is utilized to furnish iron for reducing lead sulfide, if not, iron oxide ore is added for this purpose.

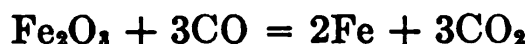
Some of the carbon in the charge reacts with some of the lead oxide to form lead and carbon dioxide.



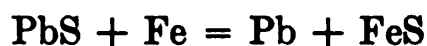
Most of the remaining carbon burns to carbon monoxide which reduces the rest of the lead oxide.



and also the iron oxide



The iron formed in this way reacts with the lead sulfide of the raw ore to form metallic lead and ferrous sulfide.



Any copper in the ore is dissolved by the ferrous sulfide to form a matte which may be smelted for the copper.

The lead tapped from the blast furnace is far from pure. It is called **work lead** or **base bullion** and contains besides the gold and silver of the ore, considerable quantities of antimony, bismuth, copper, and other impurities. Most of the latter can be removed by melting the lead in large pots and keeping it molten for several hours, during which period it is frequently stirred. The impurities oxidize more readily than the lead and the oxides rise to the top as a scum or dross, which is easily skimmed off. Some lead is lost by this process, but the resulting refined product is quite soft and malleable.

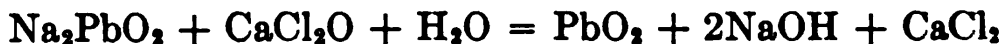
This process does not remove gold and silver or all the copper. If these are in the lead, it is further treated by the Parke Process (see p. 379) to recover the gold and silver.

Not only does the lead smelting process save the gold and silver occurring in the lead ores, but it also allows the smelting of other gold and silver ores containing little or no lead, with the lead ores, to recover the precious metals and the lead.

Lead is being successfully purified on a large scale by the Betts' electrolytic process. The anodes are made of work lead, the cathodes of pure lead and the electrolyte of lead fluosilicate,  $\text{PbSiF}_6$ , in solution to which a little glue has been added. This latter addition has the effect that the lead is deposited in a more coherent form than in its absence. The process produces very pure lead and at the same time recovers the precious

seems to have a specific action in protecting iron from corrosion. It is further used in the manufacture of glass.

**Lead Dioxide.**—Lead dioxide is the most stable and important of the tetravalent compounds of lead. It is a dark brown powder which may be formed as described above, but is usually prepared by the action of bleaching powder upon a solution of lead plumbite,



The dioxide is insoluble under these conditions and is precipitated. It has some tendency to act as an acid-forming oxide as is shown by the following. When fused with sodium or potassium hydroxide, it yields soluble meta-plumbates such as  $\text{K}_2\text{PbO}_3 \cdot 3\text{H}_2\text{O}$ , analogous to the meta-stannates. Red lead is regarded as being lead ortho-plumbate, and on this basis should be written  $\text{Pb}_2\text{PbO}_4$ .

Lead dioxide is a strong oxidizing agent. When heated with hydrochloric acid, it acts like manganese dioxide and liberates chlorine, lead chloride,  $\text{PbCl}_2$ , being formed at the same time. A few plumbic salts may be made by dissolving the dioxide in the cold concentrated acids but they all hydrolyze very easily upon dilution and reprecipitate the dioxide.

From the above it is seen that the dioxide is both basic and acidic, but is very weakly basic.

**Lead Chloride.**—Lead chloride,  $\text{PbCl}_2$ , is a white crystalline compound which is about three times as soluble in boiling water as in water at room temperature. Advantage is taken of this in qualitative analysis in separating lead chloride from silver and mercurous chlorides, which are but slightly soluble in either hot or cold water.

**Lead Nitrate.**—Lead nitrate,  $\text{Pb}(\text{NO}_3)_2$ , and acetate are almost the only lead salts of the common acids which are freely soluble in water. The nitrate is made by dissolving litharge or the metal in nitric acid, and crystallizing the product. It forms white anhydrous octahedra which are isomorphous with barium nitrate. As is to be expected from the weakness of lead hydroxide, a solution of the nitrate is acid in reaction.

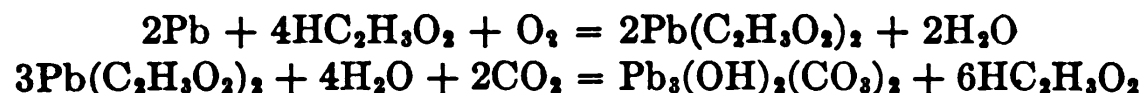
**Lead Acetate.**—Lead acetate,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ , or sugar of lead, is a white crystalline salt, which is easily soluble in water.

he solution has a sweet taste, which gives to the salt its common name. By boiling a solution of lead acetate with litharge a soluble basic salt is formed,  $\text{Pb}(\text{OH})(\text{C}_2\text{H}_3\text{O}_2)$ . This is alkaline reaction. Both the normal and the basic salts, when in solution, yield precipitates of the carbonate when acted upon by carbon dioxide; the action is not complete and stops when the concentration of the acetic acid has reached a certain point. This reaction is of importance in connection with the preparation of "white lead."

**Lead Carbonate and White Lead.**—Normal lead carbonate,  $\text{PbCO}_3$ , is found in nature as the mineral cerusite and may be prepared in the laboratory, but the artificial product is usually basic salt. Both the normal and basic salts are but very lightly soluble in water.

White lead is a basic carbonate which has approximately the composition shown by the following formula,  $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$ . It is much used as a pigment and is prepared in various ways. These nearly all consist in getting the lead in solution with acetic acid, and precipitating the carbonate with carbon dioxide, thereby recovering the acetic acid to be used to dissolve more lead and thus making it act as a catalyzer.

The white lead which is claimed to be the best is manufactured by what is known as the old Dutch process. In principle, the process consists in the solution of the lead in acetic acid, with the aid of the oxygen of the air, and the precipitation of the carbonate from this by carbon dioxide, the whole process taking place slowly at temperatures only a few degrees above that of the room. The equations are,



The lead to be "corroded" is cast into the form of perforated disks called "buckles," Fig. 69, and these are placed in the upper part of a glazed earthenware pot, about 8 in. across. In the bottom of the pot is some crude acetic acid, and about a third of the way up, the sides of the pot are pierced by a number of holes to allow circulation of air. A great number of these pots are placed side by side upon a layer of spent tan bark. They are then covered by boards and another layer of tan-bark, and upon

the whole another tier of pots is placed, which are covered in the same way. This is continued until a pile of many tiers of pots has been obtained. Bacteria grow in the tan-bark and produce carbon dioxide from the oxidation of its materials, and the heat so generated warms the whole to a temperature favorable to the process. The vapors of the acetic acid, the oxygen of the air, and the carbon dioxide from the tan-bark being in contact with the lead bring about the reactions given above. The process takes 5 or 6 weeks. At its close the heaps are taken down, the lead carbonate is separated from the unchanged lead by mechanical means and ground very fine while moist, dried, and then ground in linseed oil, making the pasty pigment known as white lead. Sometimes the white lead is not thoroughly dried

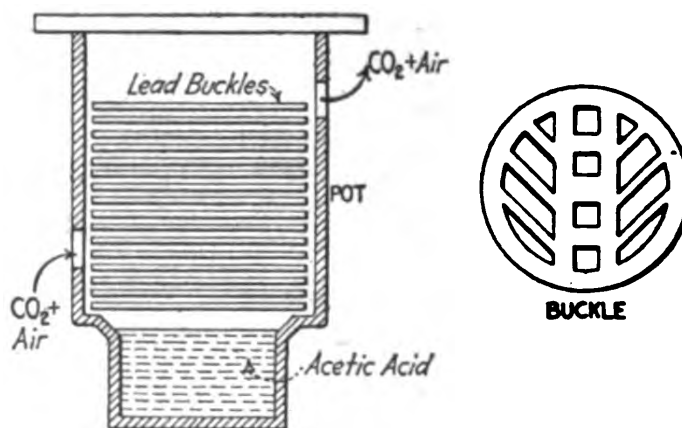


FIG. 69.

before it is ground in the oil; the result is a slightly cheaper paint of distinctly inferior quality, which is much more rapidly attacked by atmospheric agencies than that made from the dry carbonate.

White lead is costly, poisonous and hence dangerous to manufacture and use, and is so subject to atmospheric agencies, particularly hydrogen sulfide, that it is not suitable for use in cities; and yet it has held its own against other white pigments which do not have these objections. The reason for this is that it has great covering power, *i.e.*, it is very opaque. This is due to the fact that the particles of white lead, although they are transparent, reflect a good deal of light from each of their surfaces, and any given layer of paint contains so many overlying particles, each one reflecting a part of the light which penetrates

**those** above that practically all of the light is turned back, and **the** paint is decidedly opaque.

It is a well-established fact that a cheap red barn paint will **last** longer than a high-priced white house paint, when both are **mixed** with equally good oil. The explanation offered is that **the** pigment in the red paint is chemically inert, while the white **lead** in the house paint gradually converts the oil into a more or less soluble soap which washes off. The oil used in paints **must** be what is known as a "drying oil" and is usually linseed oil. A "drying oil" does not evaporate as water or gasoline does, but takes up oxygen from the air and is oxidized to a tough elastic substance which binds the pigment firmly to the painted surface. "Boiled" linseed oil has been heated with lead oxide or manganous borate, these dissolve and catalyze oxidation of the oil.

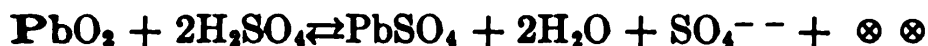
**Lead Chromate.**—Lead chromate,  $\text{PbCrO}_4$ , is insoluble and is formed by bringing together in solution a soluble lead salt and a chromate. It has a fine yellow color and is used as a pigment and as a dye under the name of chrome yellow.

**Lead Sulfate.**—Lead sulfate,  $\text{PbSO}_4$ , is one of the few sulfates which are but slightly soluble. In this respect lead resembles barium. Since it is so slightly soluble, it is easily prepared by precipitation. It is less soluble in dilute sulfuric acid and in alcohol, but more soluble in dilute nitric and in concentrated sulfuric acid than in pure water. The decrease in solubility upon the addition of dilute sulfuric acid is, of course, due to the increase in the concentration of the sulfate ion. The increased solubility in concentrated sulfuric acid is probably due to the formation of the acid sulfate. The increase in solubility in nitric acid is ascribed to the fact that nitric acid is a stronger acid than sulfuric, and hence the concentration of the sulfate ion is decreased.

A basic lead sulfate  $(\text{PbSO}_4)_2\text{PbO}$  known as sublimed white lead is used for a pigment. This compound is made by putting a mixture of finely powdered galena,  $\text{PbS}$ , and carbon on a brisk coke fire in a furnace. The lead sulfide is oxidized to the basic sulfate which volatilizes at the temperature of the fire, condenses in the flue and is caught in bags. It is very fine and white, and is chemically much more inert than white lead.

**Lead Sulfide.**—Lead sulfide,  $\text{PbS}$ , occurs in nature in cubical crystals, which have a gray metallic luster. It is the principal ore of lead and is called galena. In the laboratory it may be prepared as a black precipitate by passing hydrogen sulfide into an acid solution of a lead salt. It is insoluble in cold dilute acid, in sodium hydroxide or the alkali sulfides. It is soluble in concentrated hydrochloric acid, being reprecipitated upon dilution, and also in boiling dilute nitric acid. In the latter case, the solution results because of the oxidation of the sulfur ion to the element or to the sulfate.

**The Storage Battery.**—A storage battery is a voltaic cell, which, after it has worked for a time and produced electrical energy at the expense of the free energy of the reactions within the cell, may be restored to its original condition by passing a current of electricity through it in the reverse direction. It is a reversible cell. One of the most practical forms consists of two sets of lead plates, the one coated with lead dioxide and the other with spongy lead, the plates being placed in dilute sulfuric acid. The oxidizing agent in this case is the tetravalent lead of the lead dioxide, which gives up two positive charges to the lead electrode, upon which it is placed, and these flow through the connecting wire to the other lead electrode and there oxidize the finely divided spongy lead, which is the reducing agent, to the divalent ion. The divalent lead ion is formed at each electrode and passes into the nearly insoluble sulfate as fast as it is produced. After the cell is discharged, each electrode is coated with lead sulfate, instead of lead dioxide, or spongy lead. The cell may now be "charged" by passing a current of electricity in the reverse direction. At the anode, or dioxide plate, the divalent lead ion receives two positive charges and is changed to plumbic sulfate, which at once hydrolyzes and gives the dioxide. At the cathode, or spongy lead plate, the divalent lead ion is reduced to the metal which comes out in a spongy condition, and after somewhat more electricity has been passed through than was taken out, the cell is restored to its original condition. The excess of electricity is due to unavoidable losses. The reactions may be represented by the following equations, at the positive or dioxide plate on discharge,



in which  $\otimes \otimes$  represents the two + charges given up by the tetravalent lead and passed through the wire to the negative or spongy lead plate, where the following reaction takes place,

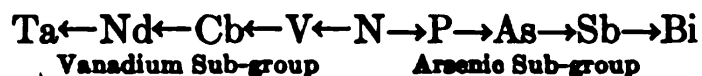


On charging, these equations are reversed.

**Analytical Properties of Lead.**—Divalent lead forms a difficultly soluble chloride which puts it in an analytical group with silver and mercurous mercury; from these it is distinguished by the solubility of lead chloride in hot water. The very slight solubility of lead sulfide in dilute acid and in alkali sulfides places it in an analytical group with mercuric mercury, copper, cadmium and bismuth. From these it is distinguished by the very slight solubility of its sulfate, all the other sulfates of the group being easily soluble. The properties of the chromate, and hydroxide are also of analytical importance.

## CHAPTER XXVII

### GROUP V



The members of Group V are polyvalent elements with a maximum valence of five. The group may be divided into two sub-groups, the first consisting of the rare and comparatively little known elements, vanadium, columbium, neodymium, and tantalum, is called the vanadium group, while the other containing the well-known elements nitrogen, phosphorus, arsenic, antimony, and bismuth may be called the arsenic group. The members of the arsenic sub-groups form a particularly well-marked family and change their properties in a very regular manner with increasing atomic weight. The tendency observed with the preceding groups for the basicity to decrease from group to group is continued here. Nitrogen and phosphorus are entirely non-metallic in their chemical and physical properties; arsenic shows principally non-metallic characteristics with some few of the properties of a metal; antimony is both a base and an acid-forming element, while bismuth is almost exclusively base-forming.

Every member of Group V forms an acidic pentoxide; the lower oxides are more basic, or at least less acidic in their tendencies.

#### VANADIUM SUB-GROUP

From the relations found in the other groups, it might be expected that the members of this family would be more basic than the corresponding ones of the arsenic group. Vanadium meets this expectation for it is distinctly more basic than arsenic; while columbium and tantalum are apparently rather more acid than base-forming elements, but their compounds have not been thoroughly studied.

These three metals all combine very vigorously with oxygen and have high melting-points.

**Vanadium**, atomic weight 51, forms five oxides,  $V_2O$ ,  $VO$ ,  $V_2O_3$ ,  $VO_2$ ,  $V_2O_5$ , analogous to the five oxides of nitrogen. The second and third of these are base-forming and yield the vanadous and vanadic salts, while the fourth and fifth are acid anhydrides and give the vanidites and vanidates respectively. It forms the following chlorides:  $VCl_2$ ,  $VCl_3$ ,  $VCl_4$ ,  $VOCl_2$  and  $VOCl_3$ . The group  $VO$  is very interesting because it acts like a complex di- and trivalent cation, forming, for example, vanadyl sulfate,  $VOSO_4$ , and di-vanadyl sulfate,  $(VO)_2(SO_4)_3$ .  $VO^{++}$  is called vanadyl and  $VO^{+++}$  di-vanadyl.

**Columbium**,  $Cb$ , atomic weight 93.5, and **tantalum**,  $Ta$ , atomic weight, 181.5, are very rare and hard to separate. Their principal compounds are the columbates and tantalates.

The atomic weight of **neodymium**, 144.3, seems to place this element in this group but its properties are very much like those of cerium with which it is always found associated in nature. As yet neither the element nor its compounds have found any applications.

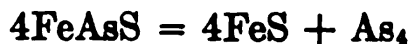
### THE ARSENIC FAMILY

The members of this family are very similar to nitrogen and especially to phosphorus; a proper grasp of their chemistry may be most readily obtained by comparison with these elements, noting the points of similarity and of difference. At the end of this chapter the whole family will be summarized in the form of a table.

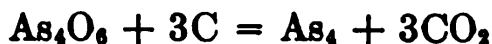
### ARSENIC

**Occurrence.**—Arsenic occurs free in nature and also in combination, chiefly in the sulfide of the metals in which it replaces a part of the sulfur, arsenical pyrite,  $FeAsS$ , may be given as an example of such a compound. It is also found as the trioxide,  $As_2O_3$ , and as the two sulfides orpiment,  $As_2S_3$ , and realgar,  $As_2S_2$ . The ores of many metals very often contain arsenic, and the removal of this element is one of the serious problems connected with their metallurgy.

**Preparation.**—The element arsenic is obtained on a manufacturing scale by heating arsenical pyrite which decomposes into ferrous sulfide and arsenic,



It may be prepared in the laboratory by reducing the trioxide with charcoal.



**Physical and Chemical Properties.**—Arsenic forms at least three solid modifications, ordinary or metallic arsenic, yellow arsenic, and a black so-called amorphous form. One of these, the ordinary or metallic arsenic is very much like red phosphorus, another, the yellow arsenic, strongly resembles yellow phosphorus. Ordinary arsenic is steel gray in color, very brittle and sublimes at  $450^\circ$  without melting. Like red phosphorus, it is not dissolved by carbon disulfide, nor does it phosphoresce in the air unless the temperature is raised. When heated, it burns forming  $\text{As}_4\text{O}_6$ . It is not attacked by acids with the evolution of hydrogen. Nitric acid, however, dissolves it forming oxides of nitrogen and arsenic acid,  $\text{H}_3\text{AsO}_4$ . It combines directly with the halogens, with sulfur and with many metals.

Yellow arsenic is made by rapidly cooling the vapor of ordinary arsenic. It is crystalline, sulfur-yellow in color and much more volatile than the ordinary form. Like yellow phosphorus, it is soluble in carbon disulfide and phosphoresces in the air at ordinary temperatures. It is even more poisonous than the metallic modification.

The molecular weight of the vapor of arsenic at temperatures below  $600^\circ$  indicates a formula of  $\text{As}_4$  while at  $1,700^\circ$  it corresponds to  $\text{As}_2$ .

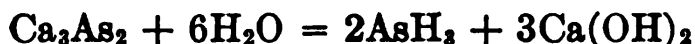
A black mirror-like modification of arsenic, which is deposited upon cooling the vapors under such conditions that the yellow is not formed, is considered to be another modification of arsenic, and was formerly held to be amorphous, but it has been shown to be crystalline.

Arsenic forms two series of compounds; in the one it is trivalent, and in the other pentavalent. There are a few compounds in which it is apparently divalent.

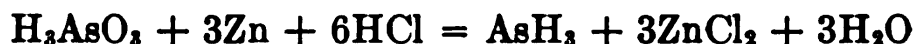
## TRIVALENT COMPOUNDS

**Arsine.**—Arsenic shows another point of similarity to nitrogen and phosphorus in the formation of the hydrogen compound arsine,  $\text{AsH}_3$ , analogous to ammonia and phosphine. It will be recalled that ammonia has a great tendency to combine with acids for the formation of ammonium salts, but that in spite of this, these salts were practically completely dissociated when in the form of vapor. Phosphine showed a much smaller tendency to form such salts and only a very few were stable, even in the solid state. If this tendency toward instability of the salts should continue to increase with the atomic weight, arsine could scarcely be expected to form any compounds of this character, and as a matter of fact none is known. Ammonia is fairly stable, but is largely decomposed at higher temperatures into its elements; phosphine is less stable and arsine still less.

Arsine may be formed by the action of water upon calcium arsenide,  $\text{Ca}_3\text{As}_2$ ,



or by the reduction of a soluble arsenic compound, arsenious acid,  $\text{H}_3\text{AsO}_3$ , for example, by zinc or magnesium, in the presence of hydrochloric or sulfuric acids,



In this case, a large amount of hydrogen is given off, but the arsine is easily obtained in the pure state by passing the mixture through a tube surrounded by liquid air. The arsine condenses to a solid, melting at  $-119^\circ$  and boiling at  $-55^\circ$ , while the hydrogen is not liquefied at this temperature.

Arsine, either pure or mixed with hydrogen, may be almost completely decomposed into its elements by passing the gas through a red hot glass tube. The arsenic is desposited beyond the burner as a black mirror. Arsine kindles easily and burns with a pale blue flame, producing water and a white smoke of arsenic trioxide. Within the flame itself the arsenic is evidently in the free state, because if a piece of porcelain or other cold object be held in the flame, a mirror of arsenic will be deposited upon it. The mirror of arsenic formed on the cold porcelain, or deposited in the glass tube beyond the burner, is so very easily

seen, even when only the merest trace of a soluble compound of arsenic is introduced into the hydrogen generator, that this test, which is known as Marsh's test, is an exceedingly valuable one. Antimony behaves in much the same way, but the two mirrors may be easily distinguished as will be seen. The zinc, acid and even the glass used must be especially pure and a "blank" experiment, run without the addition of the solution suspected to contain the arsenic, to establish their purity, must be carried out. The test is almost too delicate for ordinary work.

Arsine is exceedingly poisonous, and the inhalation of even very small quantities has produced death.

**Arsenic Trioxide.**—Arsenic trioxide, or simply arsenic, as it is usually called, is the most important compound of arsenic. It occurs in nature in small quantities, but is generally obtained by the sublimation of the flue dust from smelters which roast arsenic ores.

There are two different crystalline forms of the trioxide, octahedral and monoclinic, and also an amorphous modification. In the process of purification by sublimation the arsenic trioxide collects as an amorphous glass-like substance, which, upon being kept for some time, gradually becomes milk white and looks very much like porcelain. The change in appearance is due to the passage of the amorphous into a crystalline (octahedral) modification. It is not very soluble in water, (about 2 gm. per 100 of water at 25°). As usual the amorphous is more soluble than the crystalline.

The vapor density of the trioxide at temperatures near 600° corresponds to the formula  $As_4O_6$  and on this account it is sometimes called the hexoxide, but at 1,800° the formula indicated is  $As_2O_3$ , and this simpler one is that generally used.

The trioxide is very easily reduced by charcoal or by potassium cyanide with the formation of the metal. It acts both as an acid- and as a base-forming oxide, but is only slightly basic. With concentrated sulfuric or hydrochloric acid, it forms complicated sulfates or the trichloride,  $AsCl_3$ . These salts are completely hydrolyzed upon dilution with much water. The trioxide is highly poisonous, but if taken in repeated small doses, the system becomes accustomed to the substance and quantities may be taken with safety which would ordinarily be fatal.

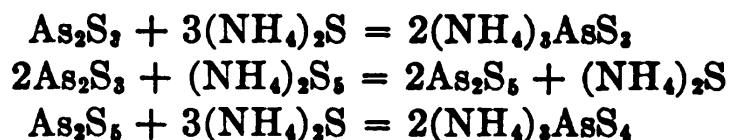
**Arsenious Acid.**—A solution of arsenic trioxide in water is slightly acid, and is called arsenious acid. When attempts are made to obtain the acid in the anhydrous state, it decomposes into water and the trioxide. The trioxide is easily soluble in sodium hydroxide solution, and from this sodium arsenite,  $\text{Na}_2\text{AsO}_3$ , may be obtained. This sodium arsenite is an important article of commerce and is used for making sheep "dips" as well as for manufacturing and chemical purposes. Like all other arsenic compounds, it is very poisonous. The arsenites of most of the metals, other than the alkalies are but slightly soluble. London purple, impure calcium arsenite and arsenate obtained as a byproduct in the manufacture of analine dyes, and Paris green, a copper acetate and arsenite,  $\text{Cu}_2(\text{C}_2\text{H}_3\text{O}_2)(\text{AsO}_3)$ , are used as insecticides, and Scheele's green,  $\text{CuHAsO}_3$ , is sometimes, though rarely at the present day, used as a pigment. It is objectionable on account of its poisonous nature. Ferric hydroxide forms very difficultly soluble arsenites, and is used as an antidote in cases of poisoning with arsenic trioxide or its salts. The arsenites are easily oxidized to the arsenates.

**The Halogen Compounds.**—Arsenic trichloride,  $\text{AsCl}_3$ , is the most important halogen compound of arsenic. It is a colorless, oily liquid, boiling at  $130^\circ$ . It may be formed by the action of chlorine upon arsenic, or by hydrochloric acid upon the trioxide. When dissolved in water, it undergoes very extensive hydrolysis with the formation of hydrochloric acid and arsenious acid, which in turn is largely decomposed into the slightly soluble trioxide and water. This action is much like that between phosphorous trichloride and water, with the exception that the hydrolysis of the arsenic compound is reversed by the addition of concentrated hydrochloric acid. Because of this, the trioxide is more soluble in hydrochloric acid than in water. Because of the volatility of arsenic trichloride, precautions have to be taken before the evaporation of an acid solution of arsenic containing chlorine as ion to see that the arsenic is oxidized to the pentavalent form, and that no reduction takes place during the process. Arsenic trifluoride is a colorless liquid, while the bromide and iodide are solids.

**Arsenic Trisulfide.**—Arsenic trisulfide,  $\text{As}_2\text{S}_3$ , is found in nature in the mineral called orpiment, which, upon being ground, yields

a lustrous yellow powder, which was formerly used as a pigment. It may be prepared in the laboratory by passing hydrogen sulfide through an acid solution of an arsenite, or of arsenious acid. Under these conditions, it comes down promptly as a flocculent yellow precipitate. If the hydrogen sulfide is passed through a pure solution of arsenious acid, no precipitate will appear, but the solution becomes yellow in color, and contains the sulfide in colloidal solution in the form of very small particles, as is shown by the fact that the path of a ray of light through the solution is visible, and the solution polarizes light. The addition of acids and of neutral salts will cause the particles to gather into flocks and to precipitate. In bringing about this result, the salts are more active the higher the valence of the cation, but the anion is almost without influence.

The sulfide is practically insoluble in even the strongest cold hydrochloric acid, but it is slowly dissolved by boiling concentrated hydrochloric acid with a volatilization of arsenic trichloride. Strong HCl and KClO<sub>3</sub> will dissolve it with the formation of arsenic acid, H<sub>3</sub>AsO<sub>4</sub>, sulfuric acid and reduction products of the chlorate. It is soluble in the alkali sulfides, giving thioarsenites (NH<sub>4</sub>)<sub>3</sub>AsS<sub>3</sub>, if the sulfide is colorless; or thioarsenates, (NH<sub>4</sub>)<sub>3</sub>AsS<sub>4</sub>, if a polysulfide is used. The equations are



The corresponding sulfides of sodium and potassium will, of course, give sodium or potassium thioarsenites, or thioarsenates. The extra sulfur of the polysulfide is the oxidizing agent, which changes the trisulfide to the penta-, which is then dissolved to form the thioarsenate. When an acid is added to one of these solutions, thioarsenious or thioarsenic acid is formed. Each of these at once decomposes evolving hydrogen sulfide and precipitating a trisulfide from the thioarsenious acid, or the pentasulfide, As<sub>2</sub>S<sub>5</sub>, from the thioarsenic acid. This behavior of the sulfide toward alkali sulfides is very much like that of the sulfides of tin and puts arsenic and tin into the same analytical group.

**Colloidal Solutions.**—Colloidal solutions have been repeatedly mentioned, and in each case it has been pointed out that they are visibly heterogeneous when a powerful beam of light passing through them is viewed by a microscope, at right angles to the light. The minute particles in suspension are seen as points of light in a ceaseless dance called the Brownian movement. As was explained on p. 75, this movement is supposed to be due to the hammering of the molecules of the liquid upon the suspended solute. Every solid or non-miscible liquid when exposed to water takes on an electric charge either positive or negative depending upon which kind of ion it adsorbs in the greater amount. Most colloids become negatively charged, but the hydroxides of the metals are positive. These charges on the colloid help to hold the particles apart and to keep the solute in suspension. If in any way these charges are neutralized, the particles collect together and soon settle out as a precipitate.

Arsenic sulfide is a negatively charged colloid, and the neutral salts precipitate it because the sulfide adsorbs enough of the cation to neutralize its negative charge; and then the particles gather together like newly churned butter until they are large enough to filter out.

It will be remembered that colloids are almost without effect upon the boiling- and freezing-point of the solvent.

### PENTAVALENT COMPOUNDS

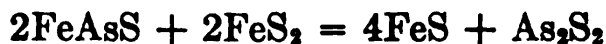
**Arsenic Pentoxide and Arsenic Acid.**—When arsenic or the trioxide is treated with concentrated nitric acid, a solution is obtained from which, after high concentration, a hemihydrate of orthoarsenic acid,  $2\text{H}_3\text{AsO}_4 \cdot \text{H}_2\text{O}$ , crystallizes. This acid is a white very soluble and deliquescent substance. Like phosphoric acid, to which it is analogous, it is tribasic and forms three series of salts. The soluble normal salts are like the corresponding phosphates in that they are largely hydrolyzed and their solutions are highly alkaline. When the orthoarsenic acid is heated, it loses water and passes into the pentoxide,  $\text{As}_2\text{O}_5$ . When orthophosphoric acid is heated, the loss of water stops with the formation of metaphosphoric acid and does not go so far as to form the pentoxide.

The orthophosphates and the orthoarsenates are isomorphous and have about the same solubilities, so that it is not altogether an easy matter to distinguish between the two groups of salts. The sharpest distinction rests upon the fact that arsenic forms a difficultly soluble sulfide with hydrogen sulfide in acid solutions, while phosphorus does not.

Sodium arsenate,  $\text{Na}_2\text{HAsO}_4$ , and the bi- or pyroarsenate,  $\text{Na}_4\text{As}_2\text{O}_7$ , have become important articles of commerce, being used to prepare the lead arsenates,  $\text{Pb}_3(\text{AsO}_4)_2$  or  $\text{PbHAsO}_4$ , which are extensively employed as sprays to protect fruit trees from the attacks of insects.

**Pentasulfide.**—Arsenic pentasulfide is a yellow powder, which may be obtained, as mentioned above, by acidulating a solution of a thioarsenate. It is also prepared by passing a rapid stream of hydrogen sulfide into a solution of arsenic acid in concentrated hydrochloric acid. It is a rather unstable substance, readily decomposing into the trisulfide and sulfur and having about the same solubilities as the trisulfide. In dissolving in the alkali sulfides, thioarsenates are formed whether the sulfide be colorless or yellow.

**Divalent Compounds.**—The best known of these compounds are the iodide,  $\text{AsI}_2$ , and the sulfide,  $\text{As}_2\text{S}_2$ . The latter occurs in nature and is known as realgar. It has a red color, melts easily, and burns to arsenic trioxide and sulfur dioxide. It may be made by heating together arsenical pyrite and pyrite,



## ANTIMONY

**Occurrence.**—Very small quantities of antimony are found free in nature. The principal ore is a trisulfide or stibnite,  $\text{Sb}_2\text{S}_3$ . From stibnite the metal is prepared either by fusion with metallic iron, which yields antimony and ferrous sulfide, or the ore is first roasted, forming sulfur dioxide and antimony tetroxide,  $\text{Sb}_2\text{O}_4$ ; the latter is then reduced by carbon. The metal prepared by either of these processes is not pure and must be remelted with sodium sulfate and slag from previous operations and finally with potassium carbonate and slag.

**Properties.**—When pure, antimony is a silvery white, highly crystalline metal, which may be easily powdered and which has density of 6.7. It melts at  $630^{\circ}$  and boils at  $1,440^{\circ}$ . The vapor density indicates a mixture of  $\text{Sb}_2$  and  $\text{Sb}_4$  in the vapor at  $334^{\circ}$ . Besides the ordinary form which has just been briefly described, there is a very unstable yellow modification, corresponding to yellow phosphorus, a more stable black form, and an explosive kind which is deposited by electrolysis from concentrated solutions of the trichloride. Antimony is a constituent of several important alloys. Type metal contains two parts of lead and one part each of tin and antimony. Like most of the alloys of antimony, it expands upon solidification and hence makes sharp castings. Babbit metal contains 1.5 per cent. copper, 13 per cent. antimony, 45.5 per cent. tin and 40 per cent. lead. It is used as an antifriction metal for the bearings of machinery.

Antimony is stable in the air at ordinary temperatures, but burns when heated, forming the trioxide or tetroxide,  $\text{Sb}_2\text{O}_3$ . It combines directly with the halogens and is oxidized by nitric acid to either the trioxide or antimonious acid,  $\text{H}_3\text{SbO}_3$ , with the formation of nitrogen peroxide. Hot concentrated sulfuric acid forms the sulfate  $\text{Sb}_2(\text{SO}_4)_3$  and sulfur dioxide. Dilute sulfuric acid and hydrochloric acid are without action upon the pure metal.

Antimony forms two series of compounds; in the one it is trivalent, and in the other pentavalent. The trivalent are the more numerous and important.

### TRIVALENT COMPOUNDS

**Stibine.**—One strong point of resemblance between antimony and the preceding members of the group is the formation of the hydrogen compound, stibine,  $\text{SbH}_3$ . This is a colorless, gaseous substance, liquefying at  $-18^{\circ}$  and freezing at  $-91.5^{\circ}$ . It is very poisonous. It is formed by the action of zinc in acid solution upon a soluble antimony compound. The reaction is very similar to that for the preparation of arsine. Stibine is even more readily decomposed than arsine and may explode. When passed through a hot tube, the decomposition goes on rapidly

at  $200^{\circ}$  and the antimony is deposited as a fusible non-volatile mirror on both sides of the heated portions of the tube. The mirror of arsenic from arsine is always deposited beyond the hot part of the tube and volatilizes easily without melting.

**The Trioxide and Its Acids.**—The density of the vapor of antimony trioxide at  $1,560^{\circ}$  corresponds with the formula,  $\text{Sb}_4\text{O}_6$ , analogous to that of phosphorus or arsenic trioxides at lower temperatures. In spite of this the formula of the substance is usually written  $\text{Sb}_2\text{O}_3$ , and it is called the trioxide, rather than the hexoxide. It may be obtained by acting upon antimony with nitric acid or by heating the metal in a limited supply of air. It is a white crystalline substance which is practically insoluble in water, dilute sulfuric or nitric acid; it is soluble in moderately dilute hydrochloric or tartaric acid and in concentrated sulfuric acid and in solutions of sodium or potassium hydroxide. These properties show that it is both basic and acidic, and therefore not strong in either way. Both series of salts are largely hydrolyzed.

The hydroxide,  $\text{Sb}(\text{OH})_3$ , is a white solid which has the same solubilities as the trioxide. When the oxide or hydroxide dissolves in sodium hydroxide, sodium meta-antimonite,  $\text{NaSbO}_2$ , is formed. Antimony hydroxide is soluble in potassium hydrogen tartrate  $\text{KHC}_4\text{H}_4\text{O}_6$  or "cream of tartar," as it is often called, owing to the formation of the complex salt tartar emetic, or potassium antimonyl tartrate,  $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$ . This salt is important in medicine and also in the laboratory, since it is almost the only antimony compound which will form a clear, neutral solution. The explanation of this is found in the very small ionization of the ion,  $\text{Sb}^{+++}$  from the complex antimonyl tartrate ion,  $\text{SbOC}_4\text{H}_4\text{O}_6^-$ . The group  $\text{SbO}$  is called antimonyl and acts like a monovalent cation. The solubility of the trioxide in tartaric acid is due to the formation of antimonyl tartrate ion. Because of the weakness of the basic properties of the hydroxide, no carbonate is known and the chloride and sulfate are largely hydrolyzed with the precipitation of basic salts. When these basic salts are boiled with water, the hydrolysis becomes completed and the trioxide is formed.

**Halogen Compounds.**—The most important halogen compound is the trichloride,  $\text{SbCl}_3$ . This may be readily prepared by dis-

olving the trisulfide in strong hydrochloric acid and distilling. The water passes off first and then the trichloride. It is a white solid, melting at  $72.0^{\circ}$  and boiling at  $233^{\circ}$ . With a small quantity of water it gives a white precipitate of the oxychloride,  $\text{SbOCl}$ , which is sometimes called antimonyl chloride. With more water the compound  $\text{Sb}_4\text{O}_5\text{Cl}_2$  is formed, and when this is washed with hot water the oxide is left behind. Hydrochloric acid will reverse this hydrolysis even more readily than that of arsenic trichloride.

The trichloride is used in medicine as a caustic and technically for bronzing iron, and in dyeing as a mordant.

The trifluoride,  $\text{SbF}_3$ , forms colorless crystals, which are deliquescent and whose solution may be diluted without precipitation, owing probably to slight ionization of the salt.

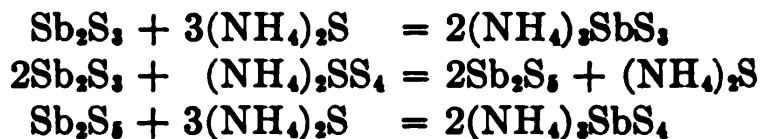
The tribromide,  $\text{SbBr}_3$ , and triiodide  $\text{SbI}_3$ , are formed in the same way as the chloride. They are easily decomposed by water.

**Other Salts.**—The salts of the oxyacids in general are not very stable and are hydrolyzed even more readily than the halogen salts. The sulfate,  $\text{Sb}_2(\text{SO}_4)_3$ , and the nitrate,  $\text{Sb}(\text{NO}_3)_3$ , may be obtained in solution, but the latter will not stand dilution and soon decomposes on standing, in spite of an excess of acid.

**Antimony Trisulfide.**—Antimony trisulfide,  $\text{Sb}_2\text{S}_3$ , is known both in the crystalline and amorphous state. The crystalline modification is black, melts at  $450^{\circ}$ , and has a metallic luster. It is found in nature and is known as stibnite; it may also be formed by heating the red amorphous form to  $220^{\circ}$ . The amorphous modification is precipitated when hydrogen sulfide is passed into an acid solution of an antimony salt. It is orange red in color and is soluble in concentrated hydrochloric acid, but is precipitated upon dilution. A method for separating arsenic and antimony may be founded upon the difference in the behavior of their sulfides toward hydrochloric acid. Arsenic sulfide is completely precipitated in very strong hydrochloric acid, while antimony is unaffected. The solution is then filtered and diluted, when, upon the passage of more hydrogen sulfide, antimony is quantitatively precipitated as the sulfide.

Antimony trisulfide is soluble in solutions of sodium or ammonium sulfide, or polysulfide, with the formation of thioantimonites with the sulfides, and thioantimonates with the

polysulfides, the reactions being strictly analogous to those for the arsenic compound;



The most common thioantimonate is that known as Schlippe's salt,  $\text{Na}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O}$ .

When the solutions of the thio salts are acidulated, thioantimonious, or thioantimonic acids are formed. These acids are unstable and promptly break down into hydrogen sulfide which escapes as a gas, and antimony tri- or pentasulfides, which are reprecipitated. The solubility of the sulfide in ammonium sulfide and its reprecipitation by acids places antimony in the analytical group with tin and arsenic.

### PENTAVALENT COMPOUNDS

The pentavalent compounds are formed from the trivalent by the action of oxidizing agents.

**Antimony Pentasulfide.**—The method for the formation of the pentasulfide has just been given in connection with the trisulfide. The oxidizing agent in this case is the polysulfide. The pentasulfide is a yellow-red substance which like the trisulfide is soluble in strong hydrochloric acid, the sulfides of ammonium, and of the alkalis. It is reprecipitated from the hydrochloric acid solution on dilution, and from the other solutions upon acidulation. The thioantimonates have already been mentioned in connection with the trisulfide.

**Antimony Pentachloride.**—Antimony pentachloride,  $\text{SbCl}_5$ , is a colorless liquid freezing at  $-6^\circ$ . It is formed when an excess of chlorine acts upon powdered antimony or by the action of chlorine upon the trichloride.

When the pentachloride is treated with a little water, various hydrates are formed, while with more water it is completely hydrolyzed, giving antimonic acid, or its anhydride, the pentoxide.

**Antimonic Acids and the Pentoxide.**—As was the case with phosphoric and arsenic acid, there are three antimonic acids. Orthoantimonic,  $\text{H}_3\text{SbO}_4$ , pyroantimonic,  $\text{H}_4\text{Sb}_2\text{O}_7$ , and metanti-

monic,  $\text{HSbO}_3$  acids. When these acids are heated they pass into the pentoxide and water. The acids and also the pentoxide are sparingly soluble in water or acids, but dissolve in potassium hydroxide. These properties indicate that the pentoxide is a purely acid-forming oxide. Potassium metantimonate,  $\text{KSbO}_3$ , is formed by fusing potassium nitrate with powdered antimony. When boiled with water it forms the acid pyro salt,  $\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7$ ,



This potassium salt is easily soluble in water, but the corresponding sodium salt requires 350 parts of water for its solution, and hence is precipitated upon the addition of a concentrated solution of the potassium salt to a strong solution of a sodium salt. This is interesting as it is one of the least soluble inorganic sodium compounds. As a test for sodium, it is far less sensitive and characteristic than the flame-test.

Antimony tetroxide,  $\text{Sb}_2\text{O}_4$ , is formed by heating the trioxide to somewhere between  $400^\circ$  and  $775^\circ$  in the air. In the absence of reducing agents it is stable up to high temperatures. It is neither an acid nor a base. One large use for the substance is in the manufacture of enamel ironware for cooking purposes. In view of the highly poisonous character of antimony compounds, this use would not seem to be wholly free from objection.

## BISMUTH

**General.**—Bismuth is far more metallic in its character than the other members of the group. The trivalent compounds are the only stable and important ones. It does not form a compound with hydrogen. Bismuth trihydroxide,  $\text{Bi}(\text{OH})_3$ , is the strongest base in the family. It does not act as an acid, and does form carbonates, nitrates, phosphates, sulfates, etc. These salts are hydrolyzed by water so the hydroxide is not a really strong base. The trisulfide does not form thio salts with the alkali sulfides.

**Occurrence and Preparation.**—Bismuth is found free in nature and to a smaller extent as the sulfide,  $\text{Bi}_2\text{S}_3$ , and oxide,  $\text{Bi}_2\text{O}_3$ . It is obtained from its ores by first roasting them to remove sulfur, and then heating in a crucible or reverberatory furnace, with

carbon to act as a reducing agent, iron to reduce unchanged sulfide, and to combine with arsenic, and fluxing material to form an easily fusible slag.

**Properties.**—Bismuth is a hard, brittle, crystalline metal with a high luster and a distinct reddish tinge of color. It has a density of 9.75, melts at  $268^{\circ}$  and boils at  $1,420^{\circ}$ . Its molecular weight lies between that required for the formulas  $\text{Bi}$  and  $\text{Bi}_2$ . The atomic weight is 208. Several alloys of bismuth, lead, tin and cadmium have been prepared, which have a melting-point below the boiling-point of water. Lipowitz metal containing 15 parts bismuth, 8 parts lead, 4 parts tin, and 3 parts cadmium, melts at  $60^{\circ}$ . Higher melting alloys are used as safety plugs in steam boilers and in making automatic fire extinguishers. Bismuth alloys expand on solidification and make good castings. Some of them are used as stereotype metal.

The metal is but very slightly acted upon in the air at ordinary temperatures, but when heated it is slowly oxidized to the trioxide. It requires a fairly strong oxidizing agent to transform it into ion, so it is not dissolved by hydrochloric acid in the absence of air. It is dissolved by hot concentrated sulfuric acid with the evolution of sulfur dioxide and also in the cold by nitric acid or aqua regia. In every case, a salt of trivalent bismuth is formed.

**Bismuth Trioxide.**—Bismuth trioxide,  $\text{Bi}_2\text{O}_3$ , is a yellow substance and is found in nature as bismuth ocher. It is made in the laboratory by heating the hydroxide, carbonate or nitrate. The trioxide has the same solubility in acids as the hydroxide, which is given below, and forms the same salts. It is not soluble in bases. The hydroxide,  $\text{Bi}(\text{OH})_3$ , is a white amorphous powder and is prepared by precipitating a bismuth salt with ammonium or sodium hydroxide. It is not soluble in excess of the base and in this way differs radically from antimony hydroxide. Acids dissolve the hydroxide with the formation of salts, such as the trichloride,  $\text{BiCl}_3$ , or nitrate,  $\text{Bi}(\text{NO}_3)_3$ . When solutions of the salts are diluted, basic salts are precipitated, such as the oxychloride,  $\text{BiOCl}$ . In fact, clear solutions of bismuth salts can be prepared only in the presence of an excess of acid.

**Bismuth Salts.**—The nitrate,  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ , is the most important salt. It forms clear colorless crystals which are

soluble in dilute nitric acid, but upon dilution the solution deposits the basic salt,  $\text{BiONO}_3$ . This is called bismuth subnitrate and is largely used in medicine. The trichloride,  $\text{BiCl}_3 \cdot \text{H}_2\text{O}$ , is colorless and is soluble in dilute hydrochloric acid. It forms the very slightly soluble oxychloride upon dilution, which is so difficultly soluble that it is used in the identification and separation of bismuth. The bromide and iodide are much like the chloride. In general, all the bismuth salts are easily hydrolyzed forming basic salts. This hydrolysis may be reversed by acids.

**Bismuth Trisulfide.**—Bismuth trisulfide,  $\text{Bi}_2\text{S}_3$ , is formed by the direct union of the elements, or by the action of hydrogen sulfide upon a moderately acid solution of a bismuth salt. It is brownish-black and is not soluble in water, cold dilute acids, the soluble sulfides, or polysulfides. It is soluble in concentrated hydrochloric and hot dilute nitric acid; in the latter case the sulfur is either liberated or oxidized to the sulfate. These properties place bismuth in the analytical group containing mercuric mercury, lead, copper, and cadmium. It is distinguished from mercury by the fact that its sulfide is soluble in hot dilute nitric acid, while that of mercury is not; from lead by the slight solubility of lead sulfate in dilute sulfuric acid; and from copper and cadmium by the fact that the hydroxide of bismuth is not soluble in an excess of ammonium hydroxide, while those of the other two metals are. It is finally identified by dissolving a little of the hydroxide in a few drops of dilute hydrochloric acid and pouring the solution into water, when a white precipitate of the oxychloride will form.

**Other Compounds.**—Besides the trioxide, bismuth forms the monoxide,  $\text{BiO}$ , the tetroxide,  $\text{Bi}_2\text{O}_4$ , and the pentoxide,  $\text{Bi}_2\text{O}_5$ . A monosulfide,  $\text{BiS}$ , analogous to the monoxide, is known. Bismuth dichloride and dibromide have been prepared, but no pentachloride or bromide.

The facts collected in the following table, show that nitrogen and bismuth differ more from the other three elements than these do from one another, but that the elements taken as a whole form a well-defined family with fairly regular changes in properties as the atomic weight is increased. Some of the more striking of these changes may be summarized as follows: As the atomic weight increases, the elements change from non-

metals to metals; the melting-point, boiling-point, and density of the element rises; the boiling-point of the hydrides (except ammonia) rises; the stability of the hydrides decreases; the basic properties of the hydrides decrease; the acid properties of the oxides decrease; the basic properties of the oxides increase.

#### COMPARISON OF THE PROPERTIES OF THE ARSENIC FAMILY OF ELEMENTS

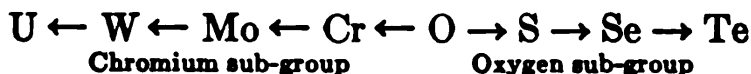
	Nitrogen	Phosphorus	Arsenic	Antimony	Bismuth
Atomic wt.....	14.01	31.04	74.96	120.2	208.0
Formulas.....	N <sub>2</sub>	P <sub>4</sub>	As <sub>4</sub> -As <sub>8</sub>	Sb <sub>4</sub> -Sb <sub>8</sub>	Bi <sub>4</sub> -Bi
Melting-point.....	- 210°	+ 44.0°	+ 480.0°	630°	268°
Boiling-point.....	- 194°	286°	450°	1,440° app.	1,420° app.
Density.....	0.89	1.8-2.3	3.9-5.7	6.7	9.75
Occurrence.....	Fr.-Cb.	Cb.-never free	Fr.-Cb.	Fr.-Cb.	Fr.-Cb.
Hydrides.....	NH <sub>3</sub>	PH <sub>3</sub>	AsH <sub>3</sub>	SbH <sub>3</sub>	.....
B.p. of hydro com.	- 33.5°	- 86°	- 55°	- 18°	.....
Comb. with acids..	Salts	Salts	.....	.....	.....
Halides.	.....	PI <sub>3</sub>	AsI <sub>3</sub>	.....	BiCl <sub>3</sub>
A = any.....	NA <sub>3</sub>	PA <sub>3</sub>	AsA <sub>3</sub>	SbA <sub>3</sub>	BiA <sub>3</sub>
halogen.....	.....	PA <sub>3</sub> *	AsF <sub>3</sub>	SbA <sub>3</sub> †	BiF <sub>3</sub>
Oxides.	.....	.....	.....	.....	.....
(ous).....	N <sub>2</sub> O <sup>1</sup>	.....	.....	.....	.....
(ic).....	NO	.....	.....	.....	BiO
(tri).....	N <sub>2</sub> O <sub>3</sub> <sup>1</sup>	P <sub>4</sub> O <sub>6</sub> <sup>1</sup>	As <sub>4</sub> O <sub>6</sub> <sup>1,2</sup>	Sb <sub>4</sub> O <sub>6</sub> <sup>1,2</sup>	Bi <sub>2</sub> O <sub>3</sub> <sup>2</sup>
(tetr).....	N <sub>2</sub> O <sub>4</sub>	P <sub>2</sub> O <sub>4</sub>	.....	Sb <sub>2</sub> O <sub>4</sub>	Bi <sub>2</sub> O <sub>4</sub>
(pent).....	N <sub>2</sub> O <sub>5</sub> <sup>1</sup>	P <sub>2</sub> O <sub>5</sub> <sup>1</sup>	As <sub>2</sub> O <sub>5</sub> <sup>1</sup>	Sb <sub>2</sub> O <sub>5</sub> <sup>1</sup>	Bi <sub>2</sub> O <sub>5</sub>
Acids.	.....	.....	.....	.....	.....
hypo-ous.....	H <sub>2</sub> N <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> PO <sub>2</sub>	.....	HSbO <sub>2</sub>	.....
meta-ous.....	HNO <sub>2</sub>	.....	HAAsO <sub>2</sub> <sup>3</sup>	H <sub>2</sub> SbO <sub>2</sub>	.....
ortho-ous.....	.....	H <sub>2</sub> PO <sub>3</sub>	H <sub>2</sub> AsO <sub>2</sub>	H <sub>2</sub> SbO <sub>2</sub>	.....
meta-ic.....	HNO <sub>3</sub>	HPO <sub>3</sub>	HAAsO <sub>2</sub> <sup>3</sup>	HSbO <sub>2</sub>	.....
pyro-ic.....	.....	H <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	H <sub>4</sub> As <sub>2</sub> O <sub>7</sub> <sup>3</sup>	H <sub>4</sub> Sb <sub>2</sub> O <sub>7</sub>	.....
ortho-ic.....	.....	H <sub>3</sub> PO <sub>4</sub>	H <sub>2</sub> AsO <sub>4</sub>	H <sub>2</sub> SbO <sub>4</sub>	.....
Sulfides.	.....	.....	.....	.....	.....
tri.....	N <sub>4</sub> S <sub>4</sub>	.....	As <sub>2</sub> S <sub>2</sub>	.....	Bi <sub>2</sub> S <sub>2</sub>
penta.....	N <sub>2</sub> S <sub>5</sub>	P <sub>2</sub> S <sub>5</sub>	As <sub>2</sub> S <sub>3</sub>	Sb <sub>2</sub> S <sub>3</sub>	Bi <sub>2</sub> S <sub>3</sub>
		P <sub>2</sub> S <sub>5</sub>	As <sub>2</sub> S <sub>5</sub>	Sb <sub>2</sub> S <sub>5</sub>	Bi <sub>2</sub> S <sub>5</sub>

\* Except PI<sub>3</sub>, which is unknown.

† Except SbBr<sub>3</sub>, which is unknown. 1 = acid forming. 2 = base forming.  
1, 2 = both acid and base forming. 3 = known only in salts.

## CHAPTER XXVIII

### GROUP VI



The members of Group VI fall naturally into two well-marked families or sub-groups; the first is called the oxygen or sulfur group and is made up of oxygen, sulfur, selenium, and tellurium. These are non-metals, although tellurium possesses some of the characteristics of the metals. Their melting- and boiling-points are comparatively low and rise regularly with the atomic weights. These elements all form compounds with the metals which are closely analogous, that is to say the oxides, sulfides, selenides, and tellurides are much alike. They all form compounds with hydrogen which are readily volatilized.

The members of the chromium family are chromium, molybdenum, tungsten, and uranium. These are all distinctly metallic, have very high boiling-points, are exceedingly hard, and do not form hydrogen compounds analogous to water, hydrogen sulfide, etc. The two sub-groups then differ markedly in some respects and the points of dissimilarity are about what would be expected from what has been noticed in the other groups. The elements of the chromium sub-group are more metallic than those of the sulfur family, have greater densities, and higher melting-points. The members of the whole sixth group have this in common that, with the exception of oxygen, they each have a maximum normal valence of six and form the oxide  $\text{RO}_3$ , in which R stands for any member of the group. Sulfur forms persulfuric acid,  $\text{H}_2\text{S}_2\text{O}_8$ , in which its valence appears to be seven and possibly chromium has this same valence in the very unstable perchromic acid. These heptavalent compounds are to be regarded as rather abnormal for the group. The oxide is in each case the anhydride of an acid. But the strength of the acid decreases as the atomic weight increases until with tellurium and uranium distinctly basic prop-

salt which is not very soluble in water, but is dissolved by strong acids. It is about the most stable of the chromous compounds.

**Chromic Compounds.**—Chromium in the chromic compounds is trivalent, and the properties of the chromic ion are very much like those of aluminum, and the trivalent iron and manganese ions. All the chromic compounds are highly colored; in solution most of them are violet and this is said to be the color of the chromic ion  $\text{Cr}^{+++}$ . Some solutions are green, but these have different chemical properties from the violet, and apparently contain complex ions. Chromium hydroxide,  $\text{Cr}(\text{OH})_3$ , is very difficultly soluble, and is precipitated when a soluble base is added to a chromic solution.

Like aluminum hydroxide, it acts as a base and as an acid, and so dissociates as follows:



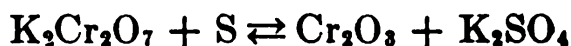
It is soluble both in acids and in excess of sodium or potassium hydroxide, forming in the first case chromic salts, and in the second chromites such as  $\text{NaCrO}_2$ . Upon standing or more quickly when boiled, a green partially dehydrated form of the hydroxide is deposited from the chromite solutions.

Ammonium hydroxide is too weak a base to dissolve chromium hydroxide with the formation of chromite, but it does dissolve it slightly owing to the formation of complex ammonia ions. Chromic hydroxide is a very weak base, and its salts, especially those of the weaker acids, are largely hydrolyzed, so the soluble sulfides precipitate chromic hydroxide instead of the sulfide. Carbonates usually precipitate the hydroxide, but under some conditions basic carbonates may be obtained. This action is much like that of aluminum salts.

Chromic oxide,  $\text{Cr}_2\text{O}_3$ , may be made by heating the hydroxide or ammonium dichromate  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ .



and also by igniting a mixture of potassium dichromate,  $\text{K}_2\text{Cr}_2\text{O}_7$ , and sulfur



The oxide has a fine green color and is used as a pigment.

**Chromic Chloride.**—Anhydrous chromic chloride is made by heating the metal in a stream of chlorine. It sublimes as peach-blossom-colored scales which are so slowly soluble in water that they are apparently insoluble; but in the presence of minute quantities of a powerful reducing agent, for example, a very little chromous chloride, solution begins and goes on so rapidly that the temperature of the system is raised several degrees, and a large amount of the chloride goes in solution, where it exists in the chromic state. Alternate reduction to the chromous and oxidation to the chromic suggests itself as an explanation for the action of the reducing agent.

The solution obtained in this way is green, and upon the addition of silver nitrate, from one- to two-thirds only of the chlorine is precipitated as silver chloride. The remainder is evidently present in complex ions. When a dilute solution of the chloride is allowed to stand for some time, it becomes violet; and then the whole of the chlorine may be precipitated by silver nitrate. The violet solution is also a better conductor of electricity than the green. By carefully evaporating a solution of the chloride, green crystals of a hexahydrate,  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ , may be obtained; under other conditions, two more modifications, one blue and the other green, each containing six molecules of water, may be prepared. When a hexahydrate is heated, it decomposes into the oxide  $\text{Cr}_2\text{O}_3$ , hydrogen chloride and water.

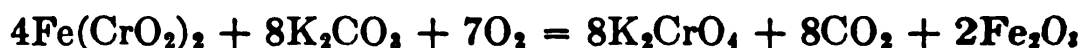
**Chromic Sulfate.**—The normal sulfate,  $\text{Cr}_2(\text{SO}_4)_3 \cdot 15\text{H}_2\text{O}$ , is violet in color, and its solution contains both the chromic and sulfate ions; but when heated, either dry or in solution, it turns green, and under certain conditions, passes into a state in which it will give reactions for neither chromic nor sulfate ions. Upon allowing the solution to stand at ordinary temperature, it slowly passes back into the violet modification. The electrical conductivity of the violet solution is much greater than that of the green under like conditions.

Chromic sulfate combines with potassium or ammonium sulfate to form the corresponding alum,  $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  or  $\text{NH}_4\text{Cr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ .

These are violet in color and are isomorphs with ordinary alum. When a solution of potassium chrome alum is boiled, it turns green and will then refuse to deposit crystals upon

cooling until it has stood for some days and changed back into the violet.

**Chromic Acid and the Chromates.**—Strong oxidizing agents in the presence of the alkalis or their carbonates will change the di- or trivalent chromium to hexavalent with the formation of chromates. Of these, perhaps, the potassium salt,  $K_2CrO_4$ , is the most important although the sodium salt is cheaper and very largely used. Potassium chromate is made by heating a mixture of chrome-ironstone, potassium carbonate and limestone in contact with the air. The equation is



The limestone is added to render the mixture porous and so assist the oxidation. The product is extracted with water, and any calcium chromate which may have formed is decomposed by the addition of potassium carbonate or sulphate.

The sodium salt is prepared in the same way using the sodium instead of the potassium carbonate. The chromates are nearly all yellow in color and have about the same solubilities as the corresponding sulfates with which they are usually isomorphous. Lead chromate is very difficultly soluble, has a brilliant yellow color and is the pigment named chrome yellow. When attempts are made to prepare chromic acid, red crystals of chromic anhydride,  $CrO_3$ , are obtained and apparently the acid,  $H_2CrO_4$ , cannot exist in the pure state.

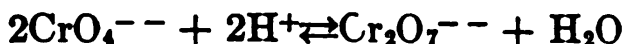
**Dichromates.**—Chromic anhydride is made by adding concentrated sulfuric acid to a solution of potassium dichromate; it crystallizes out and is washed with nitric acid. It will be recalled that sulfuric acid combined with sulfuric anhydride  $SO_3$  to form pyrosulfuric acid,  $H_2S_2O_7$ , and that this acid yields a series of salts called the pyrosulfates. In much the same way, chromic anhydride will combine with chromates forming the dichromates as they are, or pyrochromates, as they might be called.



So easily does this reaction take place and so readily is chromic anhydride formed in solution, that dichromates are made by simply acidulating solutions of the chromates. This equation may best be written ionically:



or omitting the ions which are unchanged



The reaction being reversible, it will at once be seen that acids by increasing the concentration of the  $\text{H}^+$  will cause it to go toward the right, and transform chromates into dichromates, while bases which will decrease the concentration of  $\text{H}^+$  will cause dichromates to change into chromates. The above equation will also make it clear why the difficultly soluble chromates such as barium or lead are precipitated from their soluble salts upon the addition of potassium dichromate. As fast as the chromate ion which always exists to a certain extent in any dichromate solution is used up, more is formed from the dichromate until the latter is finally practically all used up. The dichromate ion is orange red in color while the chromate is yellow; and the change of color may be used as a rough indicator of the presence of  $\text{H}^+$  or  $\text{OH}^-$ .

The tendency of chromic anhydride to combine with chromates is not exhausted with the formation of dichromate as is shown by the existence of such compounds as ammonium trichromate  $(\text{NH}_4)_2\text{Cr}_2\text{O}_{10}$ , and the tetrachromate  $(\text{NH}_4)_2\text{Cr}_4\text{O}_{12}$ .

This tendency for the formation of complex compounds is much more highly developed in molybdenum and tungsten.

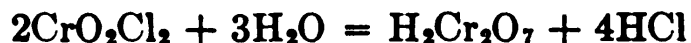
Chromates and dichromates are good oxidizing agents changing to the chromic compounds and giving up three positive charges in the transfer for each atomic weight of chromium.

Dichromates in acid solution will oxidize alcohol to aldehyde; oxalate to carbon dioxide; ferrous salts to ferric; and liberate chlorine, bromine or iodine. In either acid or alkaline solution, they will change the sulfur ion to free sulfur.

**Chromyl Chloride.**—When a mixture of a dichromate and a chloride is treated with a concentrated sulfuric acid, a dark red fuming liquid distills over which bears a striking resemblance to bromine. This is chromyl chloride,  $\text{CrO}_2\text{Cl}_2$ :



This chromyl chloride is analogous to sulfuryl chloride and like it is decomposed by water;



From this, it is seen that chromyl chloride is an acid chloride but it is interesting to note that the corresponding uranium compound,  $\text{UO}_2\text{Cl}_2$ , is a salt. This is in accord with the increase in the basic properties with the atomic weight.

**Photochemical Reactions.**—When gelatine or glue is treated with a compound of trivalent chromium, it is rendered insoluble in hot water. Use is made of this in tanning leather which contains a sort of gelatine. The chromates or dichromates do not act in this way, but if a mixture of a dichromate and glue is exposed to the sunlight, the dichromate is slowly reduced and then tans the glue. Several technically important photochemical processes are founded upon this. If a metal plate coated with a mixture of glue and ammonium dichromate is exposed under an especially prepared negative and then washed with hot water, the glue is washed away where the plate has been protected from the light, but not in the other portions. The metal plate is then treated with acids, and the parts not protected by the tanned glue are partially dissolved away. Such a plate may be inked and printed from in a regular printing press and the dark spots in the object will come dark in the print.

**Perchromic Acid.**—When hydrogen peroxide is added to an acid solution of dichromate, a very deep blue solution is obtained which soon evolves oxygen and turns green. The deep blue solution is supposed to contain perchromic acid which is thought to have the formula  $\text{HCrO}_4$ . The appearance of this blue color is a delicate test for either hydrogen peroxide or a chromate.

**Analytical Reactions of Chromium.**—All the compounds of chromium are strongly colored; chromous, generally blue; chromic, violet or green; chromate, yellow, and dichromate orange red. Chromous compounds are too unstable to require much attention. Chromic compounds are so much like those of aluminum that they fall into the same analytical group, and are precipitated by ammonium hydroxide in the presence of ammonium salts. Chromium is most readily distinguished from

iron and aluminum by the fact that its hydroxide is oxidized to sodium chromate in aqueous solution by sodium peroxide. The chromate may be recognized by its strong yellow color, by the formation of barium or lead chromate or by the blue color obtained on the addition of hydrogen peroxide to its acid solution.

### MOLYBDENUM

The rather rare element molybdenum is the second member of the chromium family. It does not occur free in nature and is found chiefly as molybdenite, the sulfide,  $\text{MoS}_2$ , and also as wulfenite or lead molybdate,  $\text{PbMoO}_4$ . When the sulfide is roasted in the air molybdenum trioxide,  $\text{MoO}_3$ , is formed. This may then be reduced to the metal by carbon in an electric furnace, by hydrogen at a high temperature, or by aluminum using the Goldschmidt process. It is a silvery white metal which is about as hard as iron. It resembles iron in that it can be forged when hot, takes up carbon and then can be tempered like steel. It is used in the form of ferro-molybdenum alloys in the manufacture of special alloy steels. The metal is scarcely affected by oxygen up to  $600^\circ$  when it forms the trioxide. It is insoluble in dilute acids, except nitric.

Molybdenum forms three oxides: the sesquioxide,  $\text{Mo}_2\text{O}_3$ ; the dioxide,  $\text{MoO}_2$ ; and the trioxide,  $\text{MoO}_3$ . The first two are basic. The chlorides of molybdenum are  $\text{Mo}_2\text{Cl}_6$ ,  $\text{MoCl}_3$ ,  $\text{MoCl}_4$ ,  $\text{MoCl}_5$ . The trioxide is the anhydride of molybdic acid,  $\text{H}_2\text{MoO}_4 \cdot \text{H}_2\text{O}$ . This forms a series of molybdates which are similar to the sulfates and the chromates not only in formula but also in solubility. Perhaps the most important of these salts, besides the naturally occurring lead compound, are the sodium and ammonium molybdates,  $\text{Na}_2\text{MoO}_4 \cdot 10\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{MoO}_4$ . The latter is much used as a reagent. Molybdic acid and its salts have a great tendency to combine with the trioxide forming complex compounds and a very large number are known. The formula of one of the sodium salts will serve to show something of the complexity of these compounds,  $\text{Na}_2\text{Mo}_{10}\text{O}_{31} \cdot 21\text{H}_2\text{O}$ .

Molybdenum trioxide will combine with other acids than molybdic acid to form complex acids. For example, it forms a series of such compounds with phosphoric acid, and these in turn

form yellow crystalline very slightly soluble salts with ammonium, potassium, rubidium and cesium in the ionic state. Because of this, when a dilute nitric acid solution of ammonium molybdate is added in excess to the solution of phosphate and the whole kept warm for some time to favor the formation of the complex phosphomolybdate ion, a yellow precipitate of ammonium phosphomolybdate,  $(\text{NH}_4)_3\text{PO}_4 \cdot (\text{MoO}_3)_{11} \cdot 6\text{H}_2\text{O}$ , separates.

The precipitate is soluble in excess of phosphoric acid or in alkalies, but is not soluble in dilute acids which implies that the phosphomolybdic acid is a strong acid. Arsenic acid and the arsenates react with the molybdates to form compounds which are very much like the phosphomolybdates in appearance and solubility.

When an acid solution of a molybdate is acted upon by a reducing agent such as hydrogen sulfide, sulfur dioxide or dilute stannous chloride, a blue solution which deposits a blue precipitate is formed. The composition of the precipitate is in doubt, but by some it is regarded as the molybdate of tetravalent molybdenum,  $\text{Mo}(\text{MoO}_4)_2$  or  $\text{Mo}_3\text{O}_8$ .

## TUNGSTEN

Tungsten is a rather rare element which has recently become of great economic importance. It occurs principally in wolfram, an iron-manganese tungstate  $(\text{FeMn})\text{WO}_4$ . In the preparation of the metal from wolfram, the ore is first heated with sodium carbonate to form sodium tungstate which is then dissolved in water. When the solution of sodium tungstate is acidulated, tungstic acid is precipitated. By gently heating the acid, it is converted into the trioxide which may be reduced to the metal in a number of ways; by carbon, hydrogen, zinc, or aluminum at rather elevated temperatures. Because of the very high melting-point of tungsten which is about  $3,500^\circ$ , the element is usually obtained in the form of a powder; but a homogeneous mass of the metal may be secured by reducing the oxide with aluminum, if an excess of powdered aluminum is used and the mixture is wet down with liquid air rich in oxygen before it is set off. The extra high temperature necessary for the fusion of the tungsten is furnished by the powdered aluminum burning in the oxygen

of the liquid air. The almost instantaneous change of temperature in this case from  $-182.5^{\circ}$  to over  $3,500^{\circ}$  is, to say the least, striking. The metal is darker colored than zinc, is crystalline, harder than glass, very brittle, and has a density of 19.6. One of the modern applications of tungsten is in the construction of high efficiency incandescent electric lamps, a use for which its very high melting-point renders it well adapted. The preparation of very fine wires required for such filaments is a matter of some difficulty, but it has been successfully done by compressing the powdered metal into rods and then rolling and drawing these down while they are heated by an electric current in an atmosphere of hydrogen. Lamps prepared from this tungsten are very durable and because of their high efficiency have almost replaced the old carbon lamps. The old style standard 16-cp. carbon lamp consumed about 60 watts. The corresponding tungsten lamp uses 25 watts and gives about 20 cp., so the tungsten lamp gives one-fourth more light on less than half the energy which means that it converts the electrical energy more efficiently into light and produces less heat. It is estimated that the replacement of the carbon lamps by tungstens has made a saving of several hundred millions of dollars per year in the country's light bill. A still further improvement has been made by filling the lamps with nitrogen or still better, argon. In these 0.5 of a watt or even a little less will give 1 candlepower.

Another important application of tungsten is in the preparation of special steels such as "high-speed steel." For this purpose a ferrotungsten is often prepared in the electric furnace. High speed steel through increasing the rate at which machines and machinists can work, has lowered the cost of automobiles on an average of \$200 per machine and made a corresponding saving in other lines. Hence tungsten is economically very important.

The metal is fairly resistant to chemical action, but when powdered it will burn at a red heat in the air. The ordinary acids act upon it very slowly, but a royal blue color is readily formed. It reacts with carbon to form the carbide,  $WC$ , from which the carbonyl,  $W(CO)_6$ , and  $W(CO)_5$ , may be obtained by reduction. It also combines with oxygen to form tungsten dioxide,  $WO_2$ , a brown powder. The tungsten trioxide,  $WO_3$ , is a yellow powder.

is used as a mordant and for rendering cotton fabric fireproof, for which purpose it is dissolved in the starch with which the articles are treated. Very complex tungstic acids and the tungstates are formed by the union of the trioxide in varying quantities with the acid or the tungstates. Compounds very similar to the phosphomolybdates are formed by the interaction of tungstic acid with phosphoric and other acids which makes the chemistry of tungsten very complex.

The atomic weight of tungsten is 184.0.

## URANIUM

Uranium, which is the last element of the chromium family, has the highest atomic weight, 238.2, of any known element. It occurs in a number of rather rare minerals, but is chiefly obtained from pitchblende which contains the oxide,  $\text{U}_3\text{O}_8$ , or carnotite which is a vanadate of uranium and potassium. These ores are interesting as furnishing the principal source of radium compounds. The metal may be prepared from the tetrachloride by reduction with metallic sodium, or from the oxide by reduction with carbon or aluminum. Pure uranium is much like iron. It has a white color, takes a high polish, has a density of 18.7, and melts at about  $1,500^\circ$ . The powdered metal is rather easily attacked chemically. It is oxidized in the air and burns in oxygen and the halogens at moderately elevated temperatures. There are two well-known oxides of uranium, the dioxide,  $\text{UO}_2$ , and trioxide,  $\text{UO}_3$ . When treated with acids, the dioxide gives a series of salts called uranous salts such as uranous chloride,  $\text{UCl}_4$ , uranous sulfate,  $\text{U}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$ , etc. The trioxide is both basic and acidic. With acids it forms a series of salts called uranyl salts. These contain the group  $\text{UO}_2^{++}$  which acts like a complex divalent cation. These salts have a yellow color and many of them have a greenish-yellow fluorescence. The most important of the uranyl salts and in fact the most important of the uranium compounds is uranyl nitrate,  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . The addition of a soluble hydroxide to a uranyl salt produces a precipitate of a diuranate, analogous to the dichromates. The sodium salt,  $\text{Na}_2\text{U}_2\text{O}_7$ , is difficultly soluble and has a fine yellow color. It is an article of com-

merce under the name uranium yellow and is used to color uranium glass which, like many other uranium preparations, has a greenish-yellow fluorescence. This phenomenon is due to the absorption of the invisible ultra-violet rays of the sunlight by the uranium compound and their conversion into visible greenish rays. Any substance which is able to become luminous, while under the excitation of some form of energy, without becoming heated to incandescence is said to be fluorescent. Fluorescence was first observed in connection with fluorspar and from this, received its name. Fluorescence differs from phosphorescence in that the former exists during the continuance of an exciting cause while the latter persists after its removal.

Metallic uranium and all of its compounds are radioactive and in fact the phenomena of radioactivity were first discovered by Becquerel in 1898 in the uranium compounds. The radioactivity of these substances is far less than that of the radium compounds and is about the same as that of the thorium salts. Again we shall have to postpone a full discussion of the subject to a later point.

## CHAPTER XXIX

### GROUP VII



With the exception of fluorine, which forms no oxy-compounds, the members of the halogen family show a variety of valencies from one up to seven. Each member of the family forms a compound with hydrogen in which the halogen is monovalent. They are typical non-metallic elements.

Manganese is the only member of the family which occupies the left-hand column of Group VII in the periodic system. It continues the regularities which have been noticed in the preceding groups in that it is much more basic than the right-hand family; it is unmistakably a metal. It does not form a compound with hydrogen analogous to the hydrohalogen acids nor is it monovalent in any compound. The strongest resemblance between manganese and the halogens is found in the heptoxide,  $\text{Mn}_2\text{O}_7$ , and the corresponding permanganic acid,  $\text{HMnO}_4$ . These are analogous to chlorine heptoxide,  $\text{Cl}_2\text{O}_7$ , and perchloric acid, in fact potassium permanganate,  $\text{KMnO}_4$ , is isomorphous with potassium perchlorate,  $\text{KClO}_4$ .

Manganese has a rather large number of valencies. It is di-, tri-, tetra-, hexa-, and heptavalent and with each alteration of valence it changes its chemical relationships, and points of similarity to additional elements become prominent. This makes the chemistry of manganese somewhat complicated. It will be seen in what follows that in the divalent form it is closely related to magnesium; in the trivalent state to chromium and iron; in the tetravalent condition to tetravalent lead and tin; while the hexavalent manganese is like sulfur in the sulfates and the heptavalent resembles chlorine in the perchlorates.

**Occurrence.**—Manganese is a fairly abundant and widely distributed element. Reference to the table on p. 274 will show that it stands between barium and strontium in its abundance.

It is found chiefly in the form of the dioxide, pyrolusite,  $\text{MnO}_2$ , to which frequent reference has been made in the past since it is a much used substance. Other less abundant ores are braunite,  $\text{Mn}_2\text{O}_3$ , manganite,  $\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , hausmanite,  $\text{Mn}_3\text{O}_4$ , manganese blende,  $\text{MnS}$ , and manganese spar,  $\text{MnCO}_3$ . The metal is obtained by the reduction of its oxides with carbon in an electric furnace or more readily by their reduction with aluminum by the Goldschmidt process. Alloys of manganese with iron containing from 10 per cent. to 90 per cent. of manganese may be prepared in blast furnaces or in electric furnaces. Those containing up to 20 per cent. are called spiegeleisen while from 20 per cent. to 90 per cent. they are known as ferromanganese. These alloys are much used in the manufacture of steel. One alloy of manganese and copper containing about 30 per cent. manganese is known as manganese bronze. It possesses great tensile strength and is very hard.

**Properties.**—Pure manganese is a reddish-gray metal which is very brittle and is so hard that it will scratch glass. Its melting-point is  $1,260^\circ$ . It is readily volatilized in the electric furnace. It holds its luster in the air but is easily dissolved by acids, even by acetic, with the evolution of hydrogen and the formation of the divalent or manganous salts. When heated to a little over  $1,200^\circ$  in a stream of nitrogen it takes fire and burns, forming a nitride. In this respect it is much like magnesium.

**Divalent or Manganous Compounds.**—The manganous salts are very much like the salts of magnesium. In many cases the two series have about the same solubility and are isomorphous. The manganous salts may be prepared by dissolving the metal, the carbonate, or any of the oxides in the acid of the salt desired and heating. The manganous salts are the only ones which are stable in acid solutions and all the others pass into them. Nearly all of them have a delicate pink color which is much more pronounced in the crystals than in the solutions. The hydroxide,  $\text{Mn}(\text{OH})_2$ , is thrown down as a white precipitate when a soluble hydroxide is added to a manganous salt solution. It has about the same solubility and strength as a base as the corresponding magnesium hydroxide, and like the latter, it is soluble in ammonium salts because of the decrease in the concentration of the hydroxyl through the formation of ammonium

hydroxide. This solution quickly darkens because of the oxidation of the manganous ion to the manganic,  $\text{Mn}^{+++}$ , by the oxygen of the air and the precipitation of manganic hydroxide,  $\text{Mn}(\text{OH})_3$ , which is too weak a base to be dissolved by ammonium salts since it is even weaker than aluminum hydroxide. Manganous oxide may be prepared by gently heating the hydroxide in the absence of air. Manganous carbonate,  $\text{MnCO}_3$ , is formed as a white precipitate when a soluble carbonate is added to a manganous salt solution. It occurs in nature where it is often found in isomorphous mixture with magnesium carbonate. The precipitated carbonate, like magnesium carbonate, is soluble in ammonium salts a salt of the metal, ammonium hydroxide and carbonic acid being formed in each case.

**Manganous sulfate**,  $\text{MnSO}_4$ , usually crystallizes with  $4\text{H}_2\text{O}$ , but below  $6^\circ$  it has  $7\text{H}_2\text{O}$  and is isomorphous with ferrous sulfate, while from  $7^\circ$  to  $20^\circ$ , the hydrate contains  $5\text{H}_2\text{O}$ , and is isomorphous with copper sulfate. It forms the double salt,  $\text{K}_2\text{SO}_4 \cdot \text{MnSO}_4 \cdot 6\text{H}_2\text{O}$ , with potassium sulfate which is isomorphous with the corresponding salt of magnesium and in fact with the whole series of these double salts.

**Manganous sulfide**,  $\text{MnS}$ , is the most soluble of the sulfides of the heavy metals. Its solubility product is so great that it cannot be precipitated by hydrogen sulfide except in the presence of hydroxyl or a very large amount of an acetate such as sodium acetate. It is usually precipitated by ammonium sulfide and generally comes down as an amorphous flesh colored substance which is readily soluble in all acids, but it sometimes appears as a green powder. When exposed to the air, the sulfide oxidizes rapidly and passes back into solution as the sulfate.

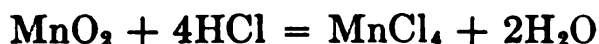
**Manganous Ammonium Phosphate**,  $\text{MnNH}_4\text{PO}_4$ , is formed under similar conditions to those for the formation of magnesium ammonium phosphate, and has closely the solubility and appearance of the latter so that it is not difficult to confuse the two.

**Manganous Borate**,  $\text{MnH}_4(\text{BO}_3)_2$ , is a salt which is of technical importance because it acts as a catalytic agent in the drying of oils and varnishes.

**Trivalent Manganese.**—The trivalent compounds of manganese or the manganic compounds as they are usually called are not as numerous nor as stable as the manganous. A solution of

the chloride may be obtained by dissolving manganic hydroxide,  $\text{Mn}(\text{OH})_3$ , in cold hydrochloric acid, but it soon evolves chlorine and passes into manganous chloride. The sulfate,  $\text{Mn}_2(\text{SO}_4)_3$ , is a violet-red powder which is very deliquescent and hydrolyzes with extreme ease with the precipitation of the hydroxide. It forms alums with rubidium and cesium sulfates. A few slightly dissociated salts, such as the fluoride,  $\text{MnF}_3$ , and the phosphate,  $\text{MnPO}_4$ , have been prepared which are not hydrolyzed. These salts give reddish-violet solutions. Manganese sesquioxide,  $\text{Mn}_2\text{O}_3$ , which is the oxide corresponding to the manganic salts occurs in nature as the mineral braunite.

**Tetravalent Manganese.**—Manganese dioxide is the principal tetravalent compound of manganese and is, in fact, the most important compound of the element. Like lead dioxide which it resembles in a number of ways, it is both feebly basic and acidic. When treated with cold hydrochloric acid it is dissolved to form the tetrachloride,  $\text{MnCl}_4$ ,



This hydrolyzes upon dilution with the precipitation of the dioxide. When heated, the tetrachloride decomposes into the dichloride and chlorine,

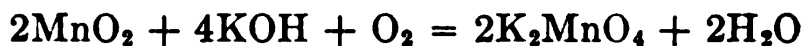


It was with the aid of these reactions that the chlorine of the world was formerly prepared, and large quantities are still made in this way although the processes involving the electrolysis of the chlorides have largely replaced it. The tetrahydroxide,  $\text{Mn}(\text{OH})_4$ , may be prepared by the action of powerful oxidizing agents upon manganous salts in neutral or alkaline solutions. In acid solutions the manganese compounds all tend to pass into the divalent state, while in alkaline solutions they tend to become tetravalent and to be precipitated as the dioxide or its hydroxide. This hydroxide is a weak acid and forms salts called the manganites of which calcium manganite,  $\text{CaMn}_2\text{O}_6$ , may be taken as an example.

Like lead dioxide, manganese dioxide is a conductor of electricity and is used as an oxidizing agent in the ordinary form of salammoniac battery known as the Leclanché cell as well as in

the slightly modified type called the dry cell. In each of these, the oxidizing agent is the dioxide and the reducing agent is metallic zinc. The dioxide is reduced to the manganous ion and the zinc oxidized to the zinc ion. The electrolyte is ammonium chloride solution containing some zinc chloride. The manganese dioxide is very slightly soluble, so it is necessary to have a very large area for the positive electrode which is of carbon packed around with the dioxide. Because of the slight solubility of the dioxide, the cell "polarizes" rapidly owing to the exhaustion of the dioxide which is in solution and in contact with the carbon electrode. It is then necessary to let the cell stand until more of the dioxide is dissolved. For this reason, the cell must be used on an open circuit. Some idea of the magnitude of the dry cell industry may be obtained from the fact that about 50,000,000 of these cells are made in this country per year.

**Hexavalent Manganese, The Manganates.**—By fusing manganese dioxide or, in fact, almost any manganese compound with potassium hydroxide in contact with the air, or more rapidly by the addition of a nitrate or chlorate, a dark green mass containing potassium manganate,  $K_2MnO_4$ , is formed;



This is soluble in water giving a green solution from which crystals may be obtained which are isomorphous with potassium sulfate. Sodium manganate crystallizes from solution with ten molecules of water,  $Na_2MnO_4 \cdot 10H_2O$ , and is isomorphous with the decahydrate of sodium sulfate. From these two examples, it will be seen that the manganates are analogous to the sulfates, and consequently hexavalent manganese to hexavalent sulfur. Solutions of manganates have an exceedingly intense green color, but are stable only in the presence of a hydroxide. Manganic acid cannot be prepared because it at once decomposes into permanganic acid and the dioxide, but its anhydride,  $MnO_3$ , has been obtained as a reddish deliquescent powder which is very unstable.

**Heptavalent Manganese, The Permanganates.**—When a solution of a manganate is diluted or acidulated, the color changes through blue and violet to purple and at the same time manganese dioxide is precipitated. The change is due to the oxida-

tion of a portion of the manganate to the permanganate at the expense of the remainder which is reduced to the dioxide,

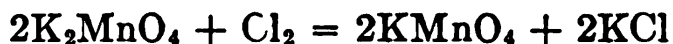


This reaction can be easily understood if the equation be written in the ionic form omitting the ions which do not enter directly into the reaction,



Since  $\text{H}^+$  is consumed in the reaction and  $\text{OH}^-$  produced, this reaction will take place much more readily when the solution is acidulated. Even a very weak acid will bring about this change, so a solution of a manganate gradually becomes purple upon exposure to the air from the absorption of carbon dioxide and the formation of carbonic acid.

The transformation of the manganate into the permanganate is oxidation and may be brought about by passing chlorine into the solution of the manganate. In this case, the chlorine is reduced to the ion  $\text{Cl}^-$  and the whole of the manganate is oxidized to the permanganate so that manganese dioxide is not precipitated,



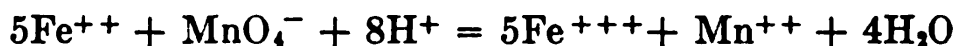
In the permanganate ion  $\text{MnO}_4^-$ , since each oxygen carries two negative charges, see p. 184, the manganese must have seven positive charges while in the manganate,  $\text{MnO}_4^{--}$ , on the same basis the manganese carries six, and in the dioxide,  $\text{MnO}_2$ , four positive charges. Then when one gram ion of the manganate is reduced to the dioxide the manganese gives up two + charges in passing from + 6 to + 4 and these two + charges are just sufficient to raise the manganese in two gram ions of the manganate from + 6 to + 7 or in other words, to oxidize them to the permanganate. Reference to the equations given above will show that this is the case, and three gram moles of manganate yield two gram moles of permanganate to one of manganese dioxide. Each atomic weight of chlorine gives up a + charge in passing into the chlorine ion  $\text{Cl}^-$ , and hence a mole of chlorine can oxidize two moles of manganate.

The permanganates are powerful oxidizing agents and disin-

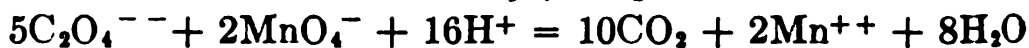
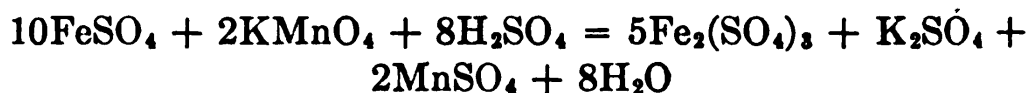
fectants and are manufactured in large quantities for such purposes. The sodium salt is the cheapest if a pure article is not demanded. It is so very soluble that it is not easily obtained pure. For laboratory purposes the potassium salt is generally used. This crystallizes well in purple crystals with a greenish luster, and is isomorphous with potassium perchlorate.

Solutions of potassium permanganate of known concentration are much used in the laboratory in the volumetric determination of easily oxidizable substances such as ferrous iron, oxalic acid or manganous salts, since the permanganate acts in a rapid and definite manner with these substances. In carrying out the operation, the permanganate solution is added from a burette to the solution to be tested and the volume necessary to give to the latter the purple color of the permanganate is noted. The operation is especially convenient since, owing to the strong color of the permanganate, no other indicator is necessary. When the permanganate is used in this way, it is reduced to the manganous ion in acid solutions or to manganese dioxide in neutral or alkaline solutions. The titration of ferrous iron or oxalic acid is carried out in acid solutions, so the manganese in passing from the heptavalent to the divalent state gives up five + charges, and hence one mole of permanganate is able to oxidize five moles of a reducing agent which takes up one + charge per mole, or two moles of the permanganate can oxidize five moles of reducing agent which takes up two + charges as is the case with the oxalate ion.

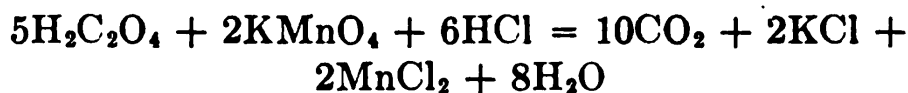
The following equations represent the reaction mentioned above,



or

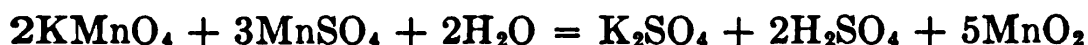


or



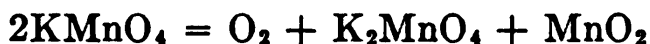
As has been mentioned, the permanganate is reduced to manganese dioxide in neutral or alkaline solutions, and also in

these same solutions, the manganous ion tends to oxidize to the tetravalent condition and to be precipitated as the dioxide. The result of these tendencies is that manganous compounds may be titrated by permanganate in neutral solutions. In going from the permanganate to the dioxide, the manganese gives up three + charges, and the manganous in going to the dioxide takes up two + charges; hence two moles of permanganate will oxidize three moles of manganous salt as shown in the following equation,



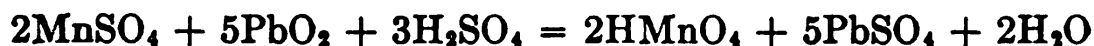
The solution tends to become acid which would interfere with the reaction, so the titration is carried on in the presence of an excess of zinc oxide which neutralizes the acid as it is formed. The behavior of permanganate as an oxidizing agent can be readily kept in mind by remembering that in acid solutions it gives up five plus charges and goes to the manganous state, while in neutral or alkaline solutions it gives up three charges and becomes manganese dioxide.

When dry potassium permanganate is heated to  $240^\circ$  it decomposes into oxygen the manganate and manganese dioxide,



This gives purer oxygen than the decomposition of the chlorate which generally yields some chlorine.

A solution of permanganic acid may be prepared by the second general method for the preparation of acids, using barium permanganate and sulfuric acid. It has the deep purple color of the permanganates and decomposes upon boiling or exposure to the light. An impure solution of the acid is also formed whenever a manganese compound is boiled with moderately dilute sulfuric or nitric acid and red lead or lead dioxide. The equation in the latter case is,



Because of the strong and very characteristic color of the permanganate ion, this constitutes one of the best tests for manganese. It is necessary, however, to have the solution highly acid and to use a very small quantity of manganese as otherwise the action stops with the formation of the dioxide. Manganese

heptoxide,  $\text{Mn}_2\text{O}_7$ , is formed by dissolving potassium permanganate in cooled concentrated sulfuric acid and carefully adding water when the oxide separates as a dark reddish-brown liquid which decomposes with the evolution of oxygen and explodes at the slightest provocation.

**Analytical Properties of Manganese.**—The solubility of manganese sulfide in acids and its precipitation by ammonium sulfide puts this element in an analytical group with zinc, cobalt, and nickel. From these it is distinguished by the pink color of its sulfide, by the formation of permanganic acid as described just above, by the green mass of manganate which is formed by fusion with an alkali and a nitrate, or by the amethyst color which all manganese compounds give in a borax bead heated in the oxidizing flame.

## CHAPTER XXX

### GROUP VIII

Fe—Co—Ni

Ru—Rh—Pd

Os—Ir—Pt

An examination of Group VIII of the periodic system will show that it differs radically from the other groups in that it is made up of three families of closely related metals in which the similar elements occur side by side, and have about the same atomic weight, instead of forming a perpendicular column with widely different atomic weights. There is, however, some similarity in the perpendicular columns, particularly between the last two families.

The three sub-families of the group are:

The iron sub-group: iron, atomic weight 55.84, cobalt, atomic weight, 58.97, and nickel, atomic weight, 58.68.

The ruthenium sub-group: ruthenium, atomic weight 101.7, rhodium, atomic weight 102.9, and palladium, atomic weight 106.7.

The platinum sub-group: osmium, atomic weight 190.9, iridium, atomic weight 193.1, and platinum, atomic weight 195.2.

All the members of the group are true metals and are somewhat remarkable for the number of complex compounds which they form.

From the gradual increase in the maximum valence which has been observed in the preceding groups, it might be anticipated that the valence of the members of this group would reach eight. The only known compounds of this kind are the tetroxides of ruthenium and osmium,  $\text{RuO}_4$  and  $\text{OsO}_4$ , and osmium octofluoride,  $\text{OsF}_8$ .

### THE IRON FAMILY

Iron forms three series of compounds: the ferrates in which it is hexavalent and resembles manganese, and chromium in the

manganates and chromates; the ferric salts in which it is trivalent and is like aluminum, and trivalent chromium or manganese; and the ferrous salts in which it is divalent and resembles the metals of the magnesium groups as well as cupric, chromous, and manganous compounds. Cobalt forms two series of salts similar to the ferric and ferrous, but the cobaltous are, in general, the more stable. Nickel forms only one series of salts, the nickelous, but shows some tendencies toward higher valence in the oxide,  $\text{Ni}_2\text{O}_3$ . The members of this family are all magnetic, have high melting-points and decompose steam at a high temperature.

### IRON

**General.**—This is truly the age of iron, as may be seen from the fact that the United States alone produces yearly about 30,000,000 long tons of the metal. A moment's thought will show that our present civilization would be very different if we did not have iron and steel in such abundance. Iron has been known and used from prehistoric times. Many meteors are composed chiefly of metallic iron, and the earliest iron tools and weapons were probably made from this source. The ores of iron are easily reduced by carbon, and even very primitive peoples have known how to do this in a small way, but the production on anything like the modern scale has only been possible since the invention of the blast furnace.

**Occurrence.**—Native iron is found in meteorites, and in certain deposits in Greenland; but all that is used is obtained from compounds. The principal ores are hematite, ferric oxide,  $\text{Fe}_2\text{O}_3$ ; brown iron ore or hydrated ferric oxide,  $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ , this is also called brown hematite, bog ore or limonite; magnetite, magnetic iron oxide,  $\text{Fe}_3\text{O}_4$ ; and siderite, spathic iron or kidney ore, ferrous carbonate,  $\text{FeCO}_3$ . Hematite furnishes about nine-tenths of the ore. Another iron mineral is pyrite,  $\text{FeS}_2$ ; this is mined in large quantities and burned as a source of sulfur dioxide in the manufacture of sulfuric acid. The residue consists principally of  $\text{Fe}_2\text{O}_3$ , but is too finely powdered and contains too much sulfur to use as an ore of iron. It has recently been found that this material may be sintered in a rotary kiln similar to that used in the manufacture of Portland cement,

and brought into a suitable mechanical state; at the same time the sulfur content is reduced to a point where it is no longer objectionable. This makes what was a waste product, a valuable source of iron. More than 50,000,000 tons of iron ore are mined each year in this country, the greater part of this comes from a region around the south and west of Lake Superior. It is mined in great open pits with steam shovels, loaded directly into cars and taken to the harbors on the lake, transferred to ships and carried to the lower lakes, where it is either unloaded and smelted on the spot, or taken by train to the great iron smelters around Pittsburgh which are conveniently located with respect to the coal fields and manufacturing centers. Within recent times a number of mammoth iron and steel plants have been located on the shores of the Great Lakes, so it looks as though Pittsburgh may lose its pre-eminence in this industry. Another important iron-producing region is around Birmingham, Alabama, which has near at hand both iron ore and coal. Everything must be done as cheaply as possible because the average price of pig iron in normal times is about \$15 per long ton.

**Metallurgy of Iron.**—The manufacture of all forms of iron and steel begins with the making of cast iron in a blast furnace. This depends for its usefulness upon the fact that by properly selecting and proportioning the materials put into the furnace, the impurities in the ore and the products of the reactions may all be removed as gases or liquids, and the operation made continuous for a long time. The materials used are coke, iron ore, and limestone. The coke burns and gives the necessary high temperature, and also furnishes the requisite reducing agent, carbon monoxide. The limestone is changed to lime which reacts with the silicious impurities in the ore to form an easily fusible slag, consisting of calcium and aluminum silicates, which is removed from the bottom of the furnace in the liquid state.

A modern blast furnace is a very large affair; 80 to 100 ft. in height by about 22 ft. in greatest diameter. Its shape is approximately that of two truncated cones set base to base. It is made of steel plates and lined with very infusible silicious fire brick.

A diagrammatic sketch of a blast furnace is shown in Fig. 70. The limestone, ore and coke in the proper proportions are charged in at the top. A blast of hot dry air is blown in through 8 to 16

plant, thus freezing out the water. This helps, because the water vapor in the air would react with the coke with the formation of carbon monoxide and hydrogen and the absorption of much heat. The saving in fuel caused by drying amounts to 20 per cent. and the output of the blast furnace is increased by the same amount.

The cast iron as it comes from the blast furnace is impure and contains from 4 to 11 per cent. of foreign substances, chiefly carbon, silicon, manganese, sulfur and phosphorus. These substances lower the melting-point of the iron and make it crystalline and brittle over all ranges of temperature. Cast iron, therefore, is not suitable for any purpose which requires considerable tensile strength, but may be used for castings which will be subjected to compression without much impact. There are two varieties of cast iron—white and gray. The white kind is made by rapid cooling; it contains the carbon in chemical combination and is very hard and brittle. The gray iron is made by slow cooling. It is tougher and softer than the white and contains a large part of the carbon in the form of crystals of graphite scattered through the mass.

By removing these impurities more or less completely, the iron may be converted into steel or wrought iron and thereby acquires much more valuable properties. More than three-quarters of the pig iron manufactured is subjected to such purification processes. *The first step in each of these is to take advantage of the fact that the impurities mentioned are more easily oxidized than the iron, and hence will be eliminated before the latter is attacked in case the crude substance is exposed to oxidation.* This oxidation is done either by the oxygen of the air or by that from iron oxide. It is difficult to draw the line between wrought iron and steel because the division is arbitrary, but the following is in common usage. Wrought iron is slag-bearing, contains less than 0.12 per cent. carbon, and does not harden materially when suddenly cooled. It is made in puddling furnaces. Steel is iron which is malleable at least over some range of temperature, contains from 0.12 to 2.2 per cent. of carbon, and which when suddenly cooled, is materially hardened. It is made in Bessemer converters, open hearth furnaces, or in crucibles.

**Bessemer Process.**—Kelly, an American, invented and patented in 1852 the process of purifying molten pig iron by blowing air through it. Bessemer, an Englishman, patented in 1855 the converter or vessel best adapted to carry out the process. After litigation, the Kelly interests sold out to the Bessemer, and the process now bears the name of the latter.

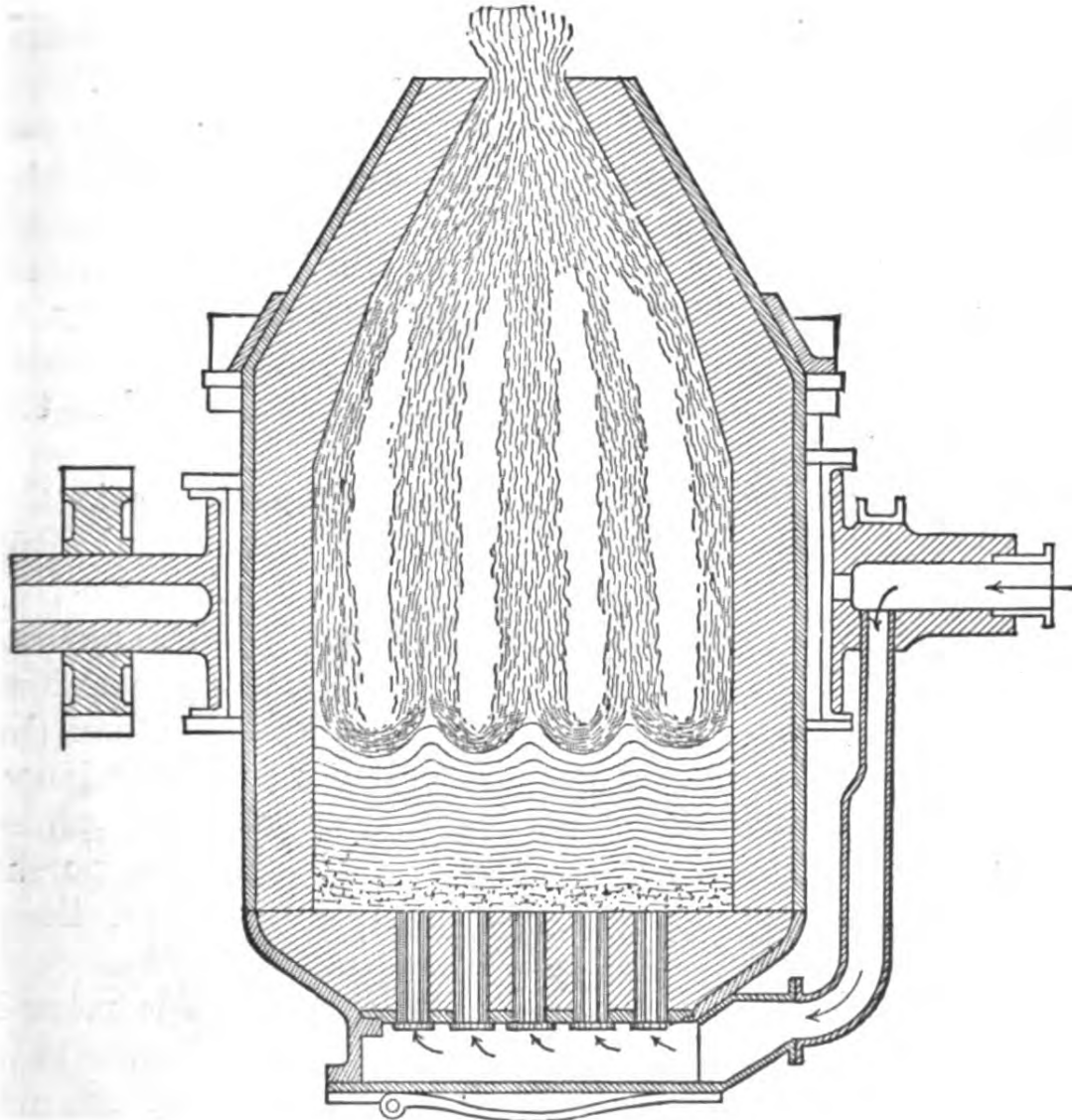


FIG. 72.

The converter used is a pear-shaped vessel, built of boiler plate and lined with silicious material, so mounted on trunions that it may be tipped through a very large angle, and provided with about 250 small holes in the bottom through which air may be blown (see Fig. 72). To start the blow, the converter is turned on its side and ten to fifteen tons of molten pig iron poured in.

The air is turned on and the converter straightened up so that the air passes through the molten iron, burning first the silicon to  $\text{SiO}_2$ , then the manganese to  $\text{MnO}$ , and lastly the carbon to  $\text{CO}$ . This burns at the mouth of the converter forming a great flame which gradually dies down and disappears at the end of the blow. The whole process is completed in from six to ten minutes. The heat produced raises the temperature some  $300^\circ$  which is favorable to the success of the operation, because removing the impurities raises the melting-point of the iron. By the time that the carbon is burned out, much of the iron is oxidized to  $\text{FeO}$ . This makes the product brittle and unfit for use. This fault is overcome by adding at the end of the blow such a quantity of spiegeleisen (an alloy of iron, manganese and carbon) as will furnish the manganese and carbon necessary to reduce the ferrous oxide and to bring the manganese, silicon, and carbon content of the whole mass to that required in the grades of steel desired.

This process using the acid or silicious lining leaves in the steel all the phosphorus and sulfur present in the pig iron. But by using basic linings made of lime or calcined dolomite,  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ , and adding lime with the charge, it is possible to remove the phosphorus and a part of the sulfur as calcium or magnesium phosphate or sulfide. The basic lining is less durable than the acid and the process more expensive, so it has been abandoned in America, although the properties of steel containing phosphorus or sulfur are so objectionable that only the purest and most expensive pig iron can be refined in acid lined converters.

After the addition of the spiegeleisen, the steel is poured out of the converter into a ladle and then tapped into cast iron moulds where it solidifies, forming ingots which are reheated and rolled into the shapes desired—rails, beams, rods, etc.

A very superior quality of steel can be produced by adding a small quantity of an alloy of iron and titanium soon after the addition of the spiegeleisen. The titanium completes the reduction of the oxides, combines with any nitrogen present, partially removes the phosphorus and sulfur, and greatly improves the strength, malleability, and toughness of the steel.

**Open Hearth or Siemens-Martin Process.**—The open hearth process for steel making is even more important than the Bessemer as may be seen from the fact that this country produces yearly 16,500,000 tons by the former as against 9,400,000 tons by the latter. This is due largely to the fact that a basic lining may be economically used in an open hearth furnace, and hence steel may be cheaply made from pig iron which contains too much phosphorus for the acid Bessemer converter.

The furnace used (see Fig. 73) is of the type known as regenerative because the air and the producer gas which is used as fuel are preheated by the waste heat of the escaping products of combustion, with the result that the temperature reached is very high.

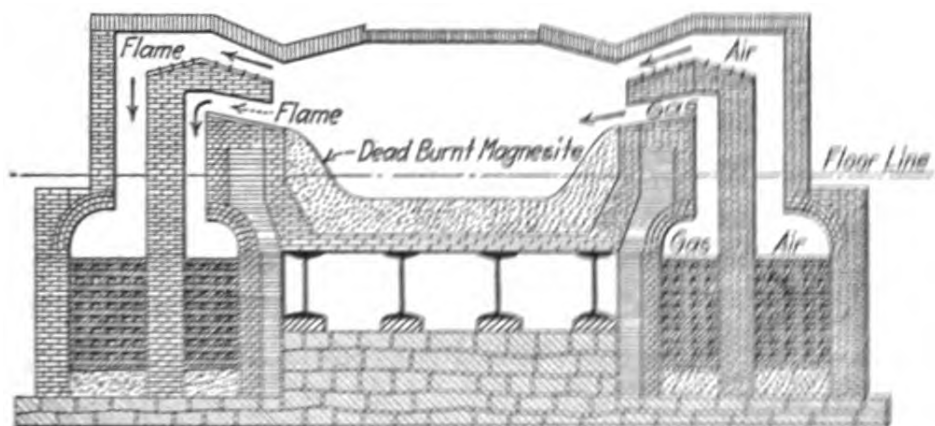


FIG. 73.

To secure these results, the air and gas are blown in separately through chambers filled with checkerwork of brick brick. They meet and burn just over the bed of the furnace containing the materials for forming the steel. The products of combustion pass out at the other end of the furnace through regenerative chambers which are displacers of the other regenerative chambers. In this way the checkerwork of brick in the air and gas chambers is intensely heated. When a new bed of material is put in the furnace the gases passing through the furnace are preheated and the heat is what had been the air and gas chambers and passing the regenerative gas. This process is continued as long as the furnace is used. The temperature of this preheating the regenerative chambers is very high. The type of furnace was invented by Siemens Brothers and applied to the production of steel in the Siemens-Martin process.

The materials used are pig iron, soft scrap steel, iron ore and in the basic process, lime. The purification of the pig iron is effected partly by an excess of air in the flame which plays over the charge, but more by the oxidizing action of the iron oxide in the ore. When the oxide is reduced, it of course increases the amount of iron present. The scrap steel is added to dilute the impurities and so hasten the process. The lime makes a very basic slag in the presence of which calcium phosphate and calcium sulfide are formed with the elimination of phosphorus and sulfur. Lime can be used only when the lining is made of calcium and magnesium oxide or the latter alone. The process is much slower than the Bessemer, requiring from six to ten hours, but the capacity of the furnace is large, usually 50 to 75 tons. Because of its slowness the changes can be followed by physical and chemical tests, and hence a more uniform and higher grade product can be produced than by the Bessemer converter. After the purification, the charge is tapped out into a ladle, slag is removed as completely as possible, and the iron recarburized to the desired degree by the addition of ferromanganese (an iron alloy rich in manganese) and anthracite coal or charcoal. It is then cast into ingots and worked up as in the other process.

The acid process is used to make about 1,200,000 tons of the 16,500,000 tons produced in the open hearth. It differs mainly in using a silicious lining and omitting the lime from the charge. The materials used must be very low in phosphorus and sulfur.

**Crucible Steel.**—By melting wrought iron with a proper amount of charcoal or cast iron in large clay or graphite crucibles, a very fine grade of high carbon steel is made which is especially desirable for making tools, knives, springs, and other special uses. The steel made by this method usually has a carbon content of from 0.75 to 1.50 per cent. and is called crucible steel.

Electric furnace steel is practically the same as crucible steel. The main difference being that melting is carried out in an electric furnace instead of a crucible, and that larger charges can be worked at a lower cost. Because of the high temperature obtainable in these, they are often used to give Bessemer or open-hearth steel a super-refining which removes phosphorus

and sulfur, and greatly improves the quality. The electricity simply serves as a source of heat and there is no electrolysis in the process.

Within recent years, it has been found that the addition of one or more of the following metals to steel will increase its valuable qualities, or impart new ones; nickel, manganese, copper, chromium, vanadium, molybdenum, tungsten, titanium, and silicon; such steels are called alloy steels, and are extensively used. Manganese steel is very tough. Nickel increases the tenacity and elastic limit. Chromium increases the hardness.

**Wrought Iron.**—A third method of purifying pig iron is the puddling process, invented by Henry Cort in 1784. This consists in melting pig iron in small lots of 500 to 1,500 lb. in a reverberatory furnace heated by coal or gas.

The hearth of the furnace is lined with roll scale or other material rich in iron oxide which with the excess oxygen in the furnace gases, serves to oxidize silicon, manganese, carbon, phosphorus and sulfur. The silica, manganous oxide, and phosphorous pentoxide produced, unite with some iron oxide formed by oxidation of iron, making a very basic slag, and effectually removing them from the iron. The melting-point of the iron which is about  $1,200^{\circ}$  in the impure state at the beginning, gradually rises as the impurities are eliminated and finally becomes so high that the pure iron cannot remain liquid at the highest temperature of the furnace. It separates, therefore, as a spongy plastic mass, honey-combed with slag. This is gathered together and worked into balls weighing about 125 lb., which are then removed from the furnace and passed through a mechanical squeezer to expel slag. The iron is rolled into rough bars, which are cut up, piled together, reheated to welding temperatures, and rolled into bars and other shapes.

The product of the puddling furnace, called wrought iron, is very nearly free from impurities, other than slag, and is the purest commercial iron.

It is very soft and malleable, welds easily, and is characterized by a fibrous structure, which easily distinguishes it from low carbon steel, which is rolled into form from cast ingots nearly free from slag. This structure is due to particles of slag enclosing those of iron and causing the iron particles to stretch separately

during the rolling process. The fibrous structure, it is thought, increases the strength of the iron.

**Physical Properties of Iron.**—Pure iron is the most magnetic of the metals. It has a density of 7.8, is silvery white, takes a high polish and is very ductile and malleable. It may be welded at a bright red heat and melts at  $1,505^{\circ}$ .

Pure iron is soft and cannot be hardened, but steel can be hardened by heating to a high temperature and suddenly cooling in water. If this hardened steel is reheated, it may be softened or tempered as it is called. The explanation is found in the fact that iron forms a carbide,  $\text{Fe}_3\text{C}$ , called cementite which is soluble to a limited extent in iron at temperatures above  $725^{\circ}$  forming solid solutions. The solubility increases with the temperature reaching 2.2 per cent. carbon at  $1,145^{\circ}$ . If these solid solutions are quickly cooled by plunging the steel into water, the cementite remains in solution, and the resulting solid solution is hard. The more cementite in the solution the harder the steel is. If this hardened steel be reheated, the cementite begins to separate and the steel gets softer. By controlling the temperature and the duration of reheating, the steel may be brought to any desired degree of hardness between that of the chilled steel and that of pure iron. The softening process may be stopped at any point by suddenly cooling the steel. Experienced workmen judge the hardness by the colors of the film of oxide on the steel which are a rough measure of the temperature to which the iron is heated.

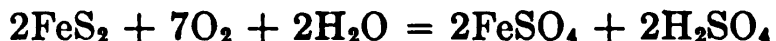
**Chemical Properties of Iron.**—Iron is stable in dry, but is attacked by moist air and gradually becomes covered with iron rust,  $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , which does not protect the underlying metal from further action. Something of a discussion of the mechanism of the rusting of iron will be given at the close of the treatment of this metal. When heated in the air or steam, iron becomes converted into the magnetic oxide,  $\text{Fe}_3\text{O}_4$ , which when formed under certain conditions clings tightly to the surface of the metal and protects it from further oxidation (Baruff's process for the prevention of rust). Dilute hydrochloric or sulfuric acids dissolve iron with the evolution of hydrogen and the formation of ferrous salts: the hydrogen usually contains some hydrocarbons as well as compounds of phosphorus and

**sulfur** and has a disagreeable odor. When the iron dissolves in cold dilute nitric acid, ferrous nitrate and ammonium nitrate are formed; while with somewhat more concentrated acid, ferric nitrate and oxides of nitrogen are produced. When iron is dipped into very concentrated nitric acid, it almost instantly becomes passive, that is passes into a condition in which it is not attacked by nitric acid, dilute or concentrated, and does not precipitate copper from cupric solutions. In fact, it acts as though it were moved in the potential series to a position near that of platinum. Potassium dichromate, chloric, bromic, iodic acids and other powerful oxidizing agents will also induce the passivity of iron. There is no visible change in the iron. The passivity is destroyed by contact with reducing agents, scratching the surface or even by simply placing the iron in a very strong magnetic field. An entirely consistent and satisfactory explanation of this phenomenon is lacking.

**Ferrous Compounds.**—The ferrous compounds are very much like those of magnesium and especially like manganous salts with the exception that the trivalent compounds of iron are more stable than the divalent either in acid or alkaline solution, while the reverse is true for manganese in acid solution. The ferrous salts even in acid solutions are oxidized in the air to ferric; in alkaline solutions, the change takes place more readily. When a perfectly pure ferrous salt solution is acted upon by a soluble base in the entire absence of oxygen, a white precipitate of **ferrous hydroxide**,  $\text{Fe}(\text{OH})_2$ , is obtained. On exposure to the air, it becomes first dirty green and finally brown from oxidation to ferric hydroxide. Ferrous hydroxide has about the solubility and strength of magnesium and manganous hydroxides and hence, like these is soluble in an excess of ammonium salts and for the same reason. It is not soluble in excess of the alkalis or of ammonium hydroxide, but is, of course, in acids. From its solubility in ammonium salts, it follows that it is a fairly strong base and its salts are but little hydrolyzed, so those of even as weak an acid as carbonic can be easily prepared. **Ferrous oxide**,  $\text{FeO}$ , corresponding to the hydroxide is most easily made by heating the oxalate in the absence of air. It has a black color.

**Ferrous Sulfate.**—Ferrous sulfate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , is the best known and most largely used of the ferrous salts. In its crude

form it is often called green vitriol or copperas. It is made on a very large scale by the oxidation of moist pyrite.



The ferrous sulfate and sulfuric acids which are formed are leached out, the acid is allowed to act on scrap iron, and the solution concentrated to crystallization. Rather large quantities of ferrous sulfate are obtained as a byproduct in plants where there is occasion to clean or "pickle" the surface of much iron by the action of sulfuric acid.

The sulfate is used as a deodorant and disinfectant, in the manufacture of dyes, in tanning, in the making of inks, and in the clarification of water.

**Ferrous Sulfide.**—Ferrous sulfide,  $\text{FeS}$ , is formed by the direct union of the elements. This takes place very readily when the two are heated together. The sulfide has a slight metallic luster. It is readily dissolved by hydrochloric or sulfuric acid with the formation of hydrogen sulfide and the corresponding ferrous salt. The usefulness of hydrogen sulfide as a reagent makes ferrous sulfide important also. It is precipitated by ammonium sulfide as a black powder easily soluble in acids, but is not precipitated by hydrogen sulfide from acid solutions.

**Other Ferrous Compounds.**—Ferrous chloride,  $\text{FeCl}_2$ , is much more soluble than ferrous sulfate, and on this account it is advisable to use hydrochloric acid instead of sulfuric in the generation of hydrogen sulfide, as the apparatus is not so likely to become clogged with crystals of the salt. There is nothing especially noteworthy concerning the bromide and the iodide except that ferrous iodide is the only stable iodide of iron, the ferric salt decomposing into the ferrous and free iodine. Ferrous carbonate occurs in nature as spathic iron ore. As it is obtained in the laboratory, it is partially hydrolyzed and is easily oxidized to the ferric hydroxide. It is more soluble in water containing carbon dioxide in solution than in pure water.

**Ferric Compounds.**—As has been mentioned, the ferric compounds are formed from the ferrous by oxidation. This takes place more readily in alkaline than in acid solutions, but the oxygen of the air is able to bring about the change in either case.

Any ferric salt in solution will be reduced to the ferrous state by the stronger reducing metals such as zinc, magnesium, iron, etc.; or by hydrogen sulfide, stannous chloride, or iodine as ion. Some of these properties are made use of in the quantitative determination of iron, it being reduced to the ferrous state and then titrated with permanganate.

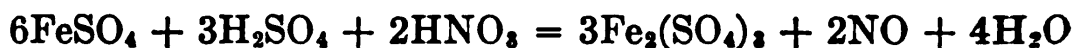
**Ferric Hydroxide.**—Solutions of bases when added to a solution of a ferric salt, produce a brown precipitate of ferric hydroxide,  $\text{Fe}(\text{OH})_3$ . This precipitate is very slimy when formed in the cold, but becomes more compact upon boiling. It has a marked tendency to pass into colloidal solution especially in the presence of ferric chloride. By separating such a solution from pure water by parchment paper, dialysis will take place and the ferric chloride will gradually diffuse into the water leaving a pure solution of colloidal ferric hydroxide. This is called dialyzed iron and has a strong red color. Like other colloids it has practically no effect upon the boiling-point of the water, and is precipitated by many neutral salts. It is a positive colloid and di- and trivalent anions are much more effective than monovalent ones. Ferric hydroxide is soluble in acids, but not in excess of dilute alkalies; or in ammonia or ammonium salts. It is a very weak base, and its salts are as highly hydrolyzed as the salts of aluminum; hence, their solutions are decidedly acid. The ferric ion appears to be colorless, but the ferric salt solutions are usually colored, presumably, in most cases, from the hydroxide formed by hydrolysis.

When the hydroxide is dried and heated, it passes into ferric oxide,  $\text{Fe}_2\text{O}_3$ , which in finely divided condition is known as "rouge" and "Venetian red," and is used as a polishing material and pigment. Although ferric hydroxide will not dissolve in dilute alkalies it is somewhat soluble in very concentrated solutions of sodium or potassium hydroxide, forming unstable ferrites. The dark colored substance formed during the early stages of the oxidation of ferrous hydroxide is probably a hydrated ferrous ferrite; and magnetic iron oxide,  $\text{Fe}_3\text{O}_4$ , is in all probability the anhydrous compound and should be written  $\text{Fe}(\text{FeO}_2)_2$ . This is a valuable iron ore and remarkable because of its being attracted by magnets. Some specimens act as magnets and are then known as lodestones. Calcium, magnesium, and zinc fer-

rites of the general formula  $M(\text{FeO}_2)_3$ , are known. These like the ferrous ferrite are magnetic.

**Ferric Chloride.**—When chlorine is passed over heated iron, anhydrous ferric chloride,  $\text{FeCl}_3$ , sublimes and crystallizes in dark green scales which have a metallic luster and are red by transmitted light. It dissolves in water with the evolution of heat and from the solution, a number of hydrates may be obtained, the most common one is  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ . This is most readily prepared, by oxidizing ferrous chloride with chlorine, evaporating the solution until it has the composition of the hexahydrate and allowing it to cool. The hydrate melts at  $37^\circ$  and is very soluble and deliquescent. Solutions of ferric chloride are considerably hydrolyzed, more so at high temperatures than at low, and react strongly acid. The chloride is soluble in alcohol and ether as well as in water. It is used in medicine.

**Ferric Sulfate.**—Ferric sulfate,  $\text{Fe}_2(\text{SO}_4)_3$ , may be prepared as a yellowish white solid by adding the proper amount of sulfuric acid to ferrous sulfate in solution and then oxidizing with nitric acid,



and evaporating to dryness. With potassium and ammonium sulfates, it forms alums such as ammonium iron alum,  $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ . When pure these are almost colorless, but generally have a violet tint due perhaps to the presence of a trace of manganese. Basic ferric sulfates are known and are used in medicine to stop the flow of blood from wounds.

**Ferric Thiocyanate.**—Ferric thiocyanate,  $\text{Fe}(\text{NCS})_3$ , is a slightly dissociated salt which is formed by the interaction of a ferric salt and a soluble thiocyanate. It has a most intense blood red color which is visible even at high dilutions. The appearance of this color upon the addition of potassium thiocyanate is a very delicate test for ferric iron. Pure ferrous compounds give no color.

**Ferric Sulfide.**—Ferric sulfide,  $\text{Fe}_2\text{S}_3$ , is thrown down as a black precipitate when a ferric salt is added to an excess of ammonium sulfide, but when the ferric salt is in excess, reduction takes place with the formation of ferrous sulfide and sulfur. Ferric sulfide is also formed by the direct union of the elements.

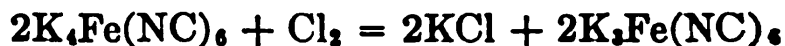
**Pyrite.**—Pyrite or "Fool's gold,"  $\text{FeS}_2$ , is the most stable of the sulfides of iron at ordinary temperatures. It is found in very large quantities in nature and is an important source of the sulfur for sulfuric acid. It occurs in golden colored crystals which appear in a great variety of forms belonging to the regular systems, cubes and octahedrons being common.

**Ferric Phosphate.**—Ferric phosphate,  $\text{FePO}_4$ , is so slightly soluble that it is precipitated upon the addition of sodium phosphate to a ferric solution even in the presence of acetic acid in which most phosphates are soluble. Advantage is sometimes taken of this property to remove the phosphate ion from solutions. It is a white slimy precipitate soluble in strong acids.

**Cyanogen Compounds.**—When potassium cyanide is added to a ferrous solution a yellow precipitate is formed which is ferrous cyanide. It dissolves in an excess of potassium cyanide, forming the typical complex salt, potassium ferrocyanide or yellow prussiate of potash,  $\text{K}_4\text{Fe}(\text{NC})_6$ . This is easily soluble in water and the solution shows the properties of other potassium salts, but not those of either the ferrous salts or the cyanides; on the contrary, it has an entirely different set of properties. The salt for example is nothing like as poisonous as potassium cyanide. This is expressed by saying that it dissociates into potassium as ion and the complex ferrocyanogen ion,  $\text{Fe}(\text{NC})_6^{4-}$ . This ferrocyanogen ion is formed whenever the ferrous ion is boiled with the cyanogen in alkaline solution. The potassium salt has the composition,  $\text{K}_4\text{Fe}(\text{NC})_6 \cdot 3\text{H}_2\text{O}$ , and the sodium,  $\text{Na}_4\text{Fe}(\text{NC})_6 \cdot 10\text{H}_2\text{O}$ . Many of the ferrocyanides are insoluble and may be prepared by precipitation. Ferric ferrocyanide,  $\text{Fe}_3(\text{Fe}(\text{NC})_6)_2$ , has a dark blue color and is known as "Prussian blue." The formation of this dark blue precipitate is a very delicate test for ferric iron and it is indeed remarkable that a solution containing iron can be used as a reagent for iron. When potassium ferrocyanide is added to a ferrous salt solution in the absence of oxygen, a white precipitate having the composition,  $\text{K}_2\text{FeFe}(\text{NC})_6$ , is formed which quickly oxidizes and becomes blue.

**Ferricyanides.**—Ferricyanides may be easily formed from the ferrocyanides by the action of oxidizing agents. The potassium

salt,  $\text{K}_3\text{Fe}(\text{NC})_6$ , for example is made by passing chloride through a solution of potassium ferrocyanide,



It crystallizes in dark red prisms and is known as "red prussiate of potash." It is the potassium salt of the complex ferricyanogen ion,  $\text{Fe}(\text{NC})_6^{--}$ , which differs from the ferrocyanogen in that it carries one less — charge. Ferric salts do not give any precipitate with ferricyanides, but the solution becomes somewhat dark brown. Ferrous salts, however, react and produce a dark blue precipitate of Turnbull's blue, ferrousferricyanide,  $\text{Fe}_2(\text{Fe}(\text{NC})_6)_2$ , which is very similar to Prussian blue. In fact, some consider it identical with Prussian blue and think that ferricyanogen oxidizes the ferrous ion to the ferric- and is itself reduced to the ferrocyanogen before they combine.

When solutions of potassium ferricyanide and ammonium ferric citrate are mixed, a yellowish-brown liquid results. If this be spread over paper and the latter dried in the dark, sensitized blue print paper results. When it is exposed to sunlight under a tracing or negative, it turns blue wherever the light strikes the paper, from the formation of insoluble blue compounds like Prussian blue. This may be due to the reduction of the ferric salt to the ferrous or of the ferricyanogen ion to the ferrocyanogen and then their interaction. After the printing, the picture is "fixed" by washing in water which dissolves the unchanged mixture, leaving white lines on a blue ground.

**Oxalates.**—Ferrous oxalate,  $\text{FeC}_2\text{O}_4$ , is precipitated as a yellow salt by the addition of oxalic acid to a ferrous solution. It is soluble in potassium oxalate owing to the formation of the complex salt,  $\text{K}_2\text{Fe}(\text{C}_2\text{O}_4)_2$ , which has a yellowish-red color not unlike that of many ferric salts. Ferric oxalate, unlike other ferric salts, has a green color remotely like that of the ferrous salts. It forms a stable complex salt with potassium oxalate,  $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3$ , which also has a green color and gives the complex ion  $\text{Fe}(\text{C}_2\text{O}_4)_3^{--}$ . The usefulness of oxalic acid and of acid potassium oxalate in removing rust and ink spots from fabrics is due to the formation of this complex ion. Solutions of ferric oxalate and of its complex compounds are very sensitive

to the light and are quickly reduced to ferrous oxalate with the evolution of carbon dioxide.

**Ferrates.**—When ferric hydroxide is suspended in potassium hydroxide solution and chlorine passed in, a red solution of potassium ferrate,  $K_2FeO_4$ , is formed. This may be obtained as crystals isomorphous with potassium sulfate and chromate. It is very unstable. Other salts have been prepared by precipitation.

**The Corrosion of Iron.**—It is, of course, well known to everyone that iron when exposed to air and water will gradually be converted into partially dehydrated ferric hydroxide, which is called iron rust. The importance of an understanding of the conditions which influence this change is obvious, owing to the almost universal use of iron in our modern structures. There is a good deal of dispute concerning many of the facts in connection with this and still more as to their interpretation, but the following observations are generally accepted as facts. First, iron will be rapidly dissolved and corroded by practically all dilute acids including carbonic, solutions of ferrous salts and hydrogen gas being the usual products. Second, iron will slowly dissolve in pure water even in the absence of oxygen or carbon dioxide. The action is not very extensive, but hydrogen gas is evolved and the solution becomes distinctly alkaline from the ferrous hydroxide which is dissolved. In the entire absence of air, the solution of ferrous hydroxide formed by the action of distilled water upon iron will remain clear; but if air be passed through it, the whole solution will take on the color of iron rust and will deposit it. Third, that the corrosion of iron will be greatly increased by the presence of oxygen. Fourth, that the iron is more readily attacked the more impure and non-homogeneous it is. Fifth, that in alkaline solutions the corrosion is greatly hindered or suppressed. Sixth, that in certain strong oxidizing agents, such as concentrated nitric acid, dichromates, and red lead, the iron becomes "passive" and will retain this condition for some time after the removal of the oxidizing agent.

The most consistent interpretation of these facts seems to be the following: That the oxidation of the iron takes place in two stages; first, to the ferrous and then to the ferric condition; that the oxidizing agent which dissolves the iron to the ferrous

state is hydrogen as ion either from acids or from water, and that the oxidation to the ferric is brought about by the oxygen of the air. Since an oxidizing agent is the more active the more concentrated it is, the more rapid solution in acids than in water is readily understood as being due to the smaller concentration of the ionized hydrogen in the latter. The protective action of alkaline solutions may be ascribed to the concentration of the hydrogen as ion having been so far reduced by the increase in the concentration of the hydroxyl that it is not a strong enough agent to oxidize the iron, and so the first stage of the rusting cannot take place.

If the iron is non-homogeneous, voltaic couples will be set up at various points on the surface and local electrolytic action will result. Hydrogen gas will be deposited at those points where the metal for any cause is acting as cathode, and since this hydrogen has a tendency to pass back into solution as ion, the local cells will be polarized and the action hindered. If oxygen is present, it will act as a depolarizer and hence increase the rate of electrolytic corrosion, and then in addition will oxidize the ferrous ion so produced to the ferric, and so complete the rusting process. There seems to be no satisfactory explanation for the passivity of iron.

**Analytical Properties of Iron.**—Because of the precipitation of ferric hydroxide by ammonium hydroxide in the presence of ammonium salts, iron is placed in an analytical group with aluminum and chromium. Ferrous salts give a deep blue with ferricyanides, while ferric compounds give the same color with ferrocyanides and also a blood red with thiocyanates. With the borax bead, iron compounds give green colorations in the reducing flame and a faint yellow or brown in the oxidizing flame.

## COBALT

Cobalt has a slightly higher atomic weight than nickel, but it is more closely related to iron than nickel is, so it is usually placed ahead of the latter in the periodic system. Cobalt occurs in nature in rather small quantities chiefly as smaltite,  $\text{CoAs}_2$ , and cobaltite,  $\text{CoAsS}$ , and is commonly associated

with iron, nickel, and manganese. It is almost always a constituent of meteoric iron and is present in the sun as indicated by the spectrum. The metal may be obtained by the reduction of the oxide at a high temperature with carbon or hydrogen, by the Goldschmidt process, or by the electrolysis of a solution of the sulfate. It is magnetic and has the color of polished iron, becoming pink on exposure to the air, and melts at  $1,494^{\circ}$ . It slowly oxidizes when heated and burns at a high temperature. It is attacked by dilute acids, but tends to become passive as iron does. Very recent experiments indicate that cobalt can be substituted with advantage for nickel in electroplating other metals. The coating may be applied much more rapidly, it is harder and more durable and hence may be made thinner than nickel with equally good results. Cobalt forms two series of compounds corresponding to ferrous and ferric. The simple cobaltous compounds are more stable than the simple cobaltic, but the case is the other way around with the complex compounds.

**Cobaltous Compounds.**—When sodium hydroxide is added to a cobaltous solution, a blue precipitate of basic salt is formed which on standing becomes pink and is changed to the hydroxide,  $\text{Co}(\text{OH})_2$ . This, like the corresponding ferrous, manganous, and magnesium compounds, is soluble in ammonium salts. In addition, it is soluble in ammonium hydroxide presumably because of the formation of complex ammonia ions. The ammoniacal solution absorbs oxygen, and a series of complex cobaltic ammonia salts are formed which will be treated briefly a little later. The cobaltous salts in dilute solution have a red color and so do most of the fully hydrated solid salts, but the partially or completely dehydrated compounds are generally blue. Cobalt chloride,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , is especially sensitive in this respect. One may prepare a dilute solution of cobalt chloride and write with it upon paper; after drying, the delicate pink of the salt is scarcely visible, but when heated it loses water and the characters become distinctly traced in the blue of the less hydrated salt. Upon standing in the air at ordinary temperatures, the salt takes up water once more and the writing disappears. This is the basis of the so-called “sympathetic ink.”

**Cobalt Sulfate.**—Cobalt sulfate,  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ , is isomorphous with magnesium sulfate and forms double sulfates with ammo-

will not be described here, but something will be said of one method in connection with nickel carbonyl.

**Properties.**—Nickel is a silvery white metal with a tinge of yellow. It takes a high polish and is hard but malleable and may be rolled into thin sheets or drawn into fine wire. The pure metal melts at  $1,451^{\circ}$ . It is magnetic. Nickel is a component of a number of important alloys. German silver contains approximately 60 per cent. copper, 25 per cent. zinc, and 15 per cent. nickel, but the composition varies widely. Nickel coins usually contain 75 per cent. copper, and 25 per cent. nickel. Nickel steel has very valuable properties because of its increased strength and toughness. A steel containing about 36 per cent. of nickel has a very small temperature coefficient and is known as "invar." It is used in making standard meters because their length will vary but slightly with the temperature. A complex wire having a core of nickel steel, a jacket of copper and a coat of platinum over all has a slightly smaller coefficient of expansion than glass and is coming into use in place of the very precious metal platinum for sealing in wires in electric light bulbs. Monel metal is a nickel-copper alloy obtained by the direct smelting of the nickel copper ores mined at Sudbury, Ontario. It can be cheaply produced and has the very valuable properties of corroding less easily than brass or bronze and of being nearly as strong as steel. Nickel may be readily deposited electrolytically from a solution of the double sulfate with ammonia  $(\text{NH}_4)_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , using anodes of cast nickel containing some carbon because they dissolve more readily than the pure metal. Iron or steel articles are first coated with copper and then with nickel. Nickel plate takes a high polish and protects the iron effectually from rust. Nickel does not rust in the air and is but slowly attacked by steam even at a red heat. It is slowly dissolved by dilute acids with the exception of nitric which acts upon it rapidly. Concentrated nitric acid, however, renders it passive.

**Nickel Compounds.**—Nickel forms only one series of salts which correspond to the ferrous and cobaltous salts. These may be considered to be derived from the oxide,  $\text{NiO}$ , or the hydroxide,  $\text{Ni}(\text{OH})_2$ , both of which are well-known. In addition there is a well-defined oxide,  $\text{Ni}_2\text{O}_3$ , and a hydroxide,  $\text{Ni}(\text{OH})_3$ , corresponding to ferric oxide and hydroxide,  $\text{Ni}_2\text{O}_4$ , analogous to

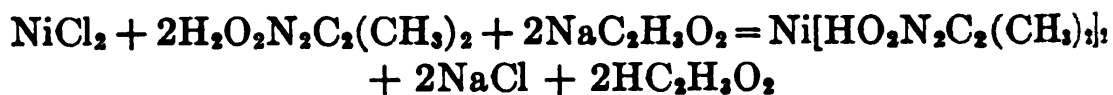
**magnetite**, and a peroxide,  $\text{NiO}_2$ , but no salts of these are known. The nickel salts both in the crystalline form and in solution are usually green.

**Oxides and Hydroxides.**—Nickelous hydroxide,  $\text{Ni(OH)}_2$ , is an apple green precipitate. When heated, it readily decomposes into water and the oxide,  $\text{NiO}$ . The hydroxide is not soluble in an excess of sodium hydroxide, but does dissolve in ammonium hydroxide owing to the formation of dark blue nickel ammoniations which probably have the composition,  $\text{Ni(NH}_3)_4^{++}$ , and  $\text{Ni(NH}_3)_6^{++}$ . The hydroxide is also soluble in ammonium salts. Nickelic oxide,  $\text{Ni}_2\text{O}_3$ , may be obtained by carefully heating the nitrate. When this or any of the other compounds of nickel is heated in oxygen, the oxide  $\text{Ni}_3\text{O}_4$  is formed. Nickelic hydroxide,  $\text{Ni(OH)}_3$ , is a black precipitate which is formed by the action of a hypochlorite on any nickel salt in solution. When nickelic hydroxide or any of the oxides, higher than the monoxide, is dissolved in hydrochloric acid, chlorine is evolved and nickelous chloride,  $\text{NiCl}_2$ , is formed.

**Edison Storage Cell.**—The Edison storage battery is a reversible, electric cell in which the oxidizing agent is nickelic hydroxide,  $\text{Ni(OH)}_3$ ; the reducing agent finely divided iron; and the electrolyte 21 per cent. potassium hydroxide. While it is discharging, the nickel is reduced to the divalent state, and the iron oxidized to the ferrous. On charge the nickel is oxidized to the nickelic, and the ferrous reduced to the metallic state, thus restoring the cell to its original condition. Its electromotive force is lower and its internal resistance higher than the corresponding magnitudes for the lead storage cell, so it is less efficient, but it is lighter and more durable than the latter.

**Salts.**—Anhydrous nickel chloride is brown, but the hexahydrate,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , is green like most of the nickel salts. The sulfate usually crystallizes as a hexahydrate,  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ , but it may be obtained as heptahydrate isomorphous with magnesium sulfate. The double sulfate with ammonium sulfate, mentioned in connection with nickel plating, is isomorphous with the other double sulfates of this same type. It is manufactured on a large scale and is one of the important salts of nickel. Nickel cyanide,  $\text{Ni(NC)}_2$ , is a green precipitate which is thrown down by potassium cyanide from a nickel salt solution.

It is soluble in an excess of the potassium cyanide forming the complex salt,  $K_2Ni(NC)_4 \cdot H_2O$ . This is not analogous to ferro- and cobaltocyanides and is much less stable. It is not oxidized to anything which corresponds to the ferri- or cobalticyanides. Nickel salts color the borax bead brown while cobalt compounds give a very intense blue. Nickel sulfide,  $NiS$ , is formed under the same conditions as that of cobalt and has the same solubility. A solution of dimethyl glyoxime  $H_2O_2N_2C_2(CH_3)_2$  reacts with a solution of a nickel salt, acid with acetic acid and containing sodium acetate, to give a bright red precipitate of nickel dimethyl glyoxime,



Cobalt does not form such a precipitate and this makes it easy to detect nickel in the presence of cobalt.

**Nickel Carbonyl.**—Nickel carbonyl,  $Ni(CO)_4$ , is formed below  $80^\circ$  by the action of carbon monoxide upon finely divided nickel. It is a colorless liquid which boils at  $43^\circ$ . Its vapor decomposes explosively at  $60^\circ$ . When diluted with carbon monoxide it decomposes gradually and its decomposition is not complete below  $180^\circ$ . Cobalt does not form any similar compound. A process based upon this property of nickel has been used for its extraction from the ores. One difficulty in its application is that the carbon monoxide is partially decomposed with the deposition of carbon and the formation of the dioxide.

## THE PLATINUM METALS

The remaining members of Group VIII, the ruthenium and platinum sub-groups may conveniently be considered together under the heading of the platinum metals. These metals are found associated in the native platinum ores which are obtained by placer mining or dredging, chiefly in the Ural Mountains, although Columbia furnishes a small per cent. of the world's output. They are also found in certain copper ores and in the nickel copper ores of Sudbury, Ontario. In the following table these metals are arranged as they are in the periodic system and

under each is given some of its more prominent properties and the formulas of a few typical compounds.

	<i>Ruthenium</i>		<i>Rhodium</i>		<i>Palladium</i>	
Density	12.0		12.1		11.5	
Melt. p.	2,000°		1,970°		1,550°	
Oxides	RuO		RhO		PdO	
	Ru <sub>2</sub> O <sub>3</sub>		Rh <sub>2</sub> O <sub>3</sub>		_____	
	RuO <sub>2</sub>		RhO <sub>2</sub>		PdO <sub>2</sub>	
	RuO <sub>4</sub> (vol. liq.)		_____		_____	
Salts	RuCl <sub>2</sub>		_____		PdCl <sub>2</sub>	
	RuCl <sub>3</sub> ,	K <sub>2</sub> RuCl <sub>6</sub>	RhCl <sub>3</sub> ,	K <sub>2</sub> RhCl <sub>6</sub>	_____	_____
	_____	_____	Rh <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	(alums)	_____	_____
	RuCl <sub>4</sub> ,	K <sub>2</sub> RuCl <sub>6</sub>	_____	_____	PdCl <sub>4</sub> ,	K <sub>2</sub> PdCl <sub>6</sub>
	K <sub>2</sub> RuO <sub>4</sub> ,	KRuO <sub>4</sub>	_____	_____	_____	_____
	<i>Osmium</i>		<i>Iridium</i>		<i>Platinum</i>	
Density	22.5		22.4		21.4	
Melt. p.	2,700°		2,200°		1,753°	
Oxides	OsO		_____		PtO	
	Os <sub>2</sub> O <sub>3</sub>		Ir <sub>2</sub> O <sub>3</sub>		_____	
	OsO <sub>2</sub>		IrO <sub>2</sub>		PtO <sub>2</sub>	
	OsO <sub>4</sub> (vol. liq.)		_____		_____	
Salts	OsCl <sub>2</sub>		IrCl <sub>2</sub>		PtCl <sub>2</sub> ,	K <sub>2</sub> PtCl <sub>4</sub>
	OsCl <sub>3</sub> ,	K <sub>2</sub> OsCl <sub>6</sub>	IrCl <sub>3</sub> ,	K <sub>2</sub> IrCl <sub>6</sub>	_____	_____
	_____	_____	Ir <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	(alums)	_____	_____
	OsCl <sub>4</sub> ,	K <sub>2</sub> OsCl <sub>6</sub>	IrCl <sub>4</sub> ,	K <sub>2</sub> IrCl <sub>6</sub>	PtCl <sub>4</sub> ,	K <sub>2</sub> PtCl <sub>6</sub>
	K <sub>2</sub> OsO <sub>4</sub>	_____	_____	_____	_____	_____

An inspection of this table will show strong resemblances between the elements in each horizontal row and vertical column. All these elements form complex compounds with ammonia which are so numerous and varied that larger works must be consulted for their discussion.

**Ruthenium** and **osmium** are iron gray metals which are not dissolved by any single acid, and are but very slowly attacked even by aqua regia. They are dissolved by fusion with alkalis and nitrates. When finely divided and heated in oxygen they form the tetroxides and volatilize. Osmium tetroxide is not the anhydride of any acid, but is called osmic acid. It is used for staining and hardening histological specimens. It has a very disagreeable odor and is exceedingly irritating to the mucous membrane owing to its reduction to metallic osmium. The formation of osmates and ruthenates establishes a connection with iron and manganese.

**Rhodium** and **iridium** are white metals which are not attacked by aqua regia. They will form very hard, chemically resistant alloys with platinum. Iridium especially is used for this purpose.

**Palladium** and **platinum** are white metals. Platinum dissolves in aqua regia and palladium even in nitric acid, and is the only metal in the two sub-groups which will do so. Both platinum and palladium are remarkable for their ability to absorb gases, especially hydrogen, of which palladium will take up as much as 1,000 times its volume. The hydrogen and the palladium form a solid solution which has greater volume than the metal. The hydrogen in this solution will readily reduce silver and copper to the metals, and ferric salts to ferrous as would be expected from the position of hydrogen in the potential series, which, of course, is not materially altered by its solution in palladium.

**Platinum.**—Platinum is by far the most important member of this group. Not only is it indispensable to the chemist, but it also touches our daily life in many ways, especially in our electrical appliances. It is almost the only pure metal which has the proper coefficient of expansion, melting-point, and chemical resistivity to enable it to be fused through glass. This comes into play in many ways, particularly in the making of incandescent electric bulbs. It is used in the form of wire, foil, crucibles, and dishes in the laboratory, and it is hard to conceive what we should do without it.

Platinum ware must be handled with care because it is ruined by contact when hot with easily fusible metals, alkalies, phosphorus, carbon, and silicon. The carbonates of the alkalies may be heated in it without danger. Aqua regia or anything which will evolve chlorine should not be allowed in contact with platinum.

As has been noticed many times on the preceding pages, platinum is very active as a catalytic agent, especially for reactions between gases. Advantage is taken of this on a large scale for the production of sulfuric acid by the contact process. The reactions take place on the surface of the metal and naturally go on more rapidly in the aggregate, the greater the surface exposed. For this reason the very finely divided black form of

**the** metal which is obtained by the electrolysis of its chloride in solution, or by the reduction of the solution with a powerful reducing agent, is especially active and will cause the instantaneous explosion of a mixture of oxygen and hydrogen. The metal may be obtained in a spongy condition with large surface and high activity by gently heating ammonium chloroplatinate,  $(\text{NH}_4)_2\text{PtCl}_6$ , which decomposes and leaves spongy platinum. By heating this platinum sponge to whiteness and then hammering, it may be converted into compact metal, for at this temperature platinum welds very easily.

**Platinum Compounds.**—As may be seen from the table, platinum forms two series of compounds. In the platinous it is di- and in the platonic tetravalent. The platinous compounds are generally formed from the platonic by reduction.

**Platinous Hydroxide.**—Platinous hydroxide,  $\text{Pt}(\text{OH})_2$ , is a black precipitate which is soluble in acids but not in bases. With hydrochloric acid it forms chloroplatinous acid,  $\text{H}_2\text{PtCl}_4$ , whose potassium salt,  $\text{K}_2\text{PtCl}_4$ , potassium chloroplatinite is used in making platinum photographic prints. Similar compounds are well known in which chlorine is replaced by cyanogen. These are called platinocyanides. The barium platinocyanide,  $\text{BaPt}(\text{NC})_4 \cdot 4\text{H}_2\text{O}$ , is very fluorescent and shines under the influence of ultra-violet light and X-rays. Advantage is taken of this in making screens for X-ray work.

When platinum dissolves in aqua regia it forms chloroplatinic acid,  $\text{H}_2\text{PtCl}_6$ , which gives sparingly soluble chloroplatinates with potassium and ammonium salts,  $\text{K}_2\text{PtCl}_6$ , and  $(\text{NH}_4)_2\text{PtCl}_6$ . These form yellow precipitates which consist of small octahedrons and are very characteristic for platinum. When heated they decompose and leave spongy platinum and potassium chloride from  $\text{K}_2\text{PtCl}_6$ , or simply platinum from the ammonium salt. When silver salts are added to solutions of the chloroplatinates, precipitates of  $\text{Ag}_2\text{PtCl}_6$ , are formed and not  $\text{AgCl}$ , which shows that the chloroplatinate ion is a stable complex ion. By heating chloroplatinic acid in a stream of chlorine, platonic chloride,  $\text{PtCl}_4$ , is formed. When dissolved in water this gives  $\text{H}_2\text{PtCl}_4\text{O}$ .

**Platonic Hydroxide.**—Platonic hydroxide,  $\text{Pt}(\text{OH})_4$ , is formed by the addition of bases to chloroplatinate solutions. It is soluble both in acids and bases. Complex platinates are formed by

the action of bases upon the hydroxide. The potassium salt may be represented by the formula,  $K_2Pt(OH)_6$ , and is considered analogous to the chloroplatinates.

**Analytical Properties of Platinum.**—Platinous sulfide,  $PtS$ , and platinic sulfide,  $PtS_2$ , are precipitated by hydrogen sulfide from the respective salts. They are not soluble in dilute acids but dissolve in yellow ammonium sulfide, forming thioplatinates. Platinum compounds are slowly reduced to the metal by ferrous salts but not by oxalic acid. This latter property is a distinction from gold.

## CHAPTER XXXI

### RADIOACTIVITY

In discussing radium, thorium, and uranium, mention was made that these substances are radioactive; and by this is meant that they spontaneously give out heat and other manifestations of energy which are able to affect a photographic plate; to cause certain substances to fluoresce; and to render the air in their neighborhood a conductor of electricity. These other manifestations of energy are called rays; and from this comes the term radioactivity. Three different kinds of these rays are distinguished; the alpha, beta, and gamma rays.

The alpha rays are responsible for most of the ionization of the air produced by radioactive substances; they can penetrate the air only a few centimeters and are easily stopped by paper. They are connected with the development of the greater part of the heat evolved by such substances. When uninfluenced by external forces they move in straight lines; but under the influence of an electrostatic or a magnetic field, they are slightly bent out of their path and act as though they consisted of a stream of rapidly moving small particles charged with positive electricity. Calculations based upon the bending of the path of the rays in these two fields indicate that 2 gm. of the rays would carry 96,500 coulombs and that they move with about one-tenth the velocity of light. These rays are generally supposed to be atoms of helium carrying two positive charges of electricity.

The beta rays are more penetrating than the alpha rays and pass readily through paper and even through thin sheets of metal. They are especially active toward a photographic plate. Like the alpha rays they move in a straight line, unless influenced by a magnetic or electrostatic field when they are deflected in the opposite direction from that in which the alphas are turned and much more strongly. They act like negatively charged particles, and calculations based upon this assumption indicate that 1 gm.

of beta rays would carry  $1,800 \times 96,500$  coulombs and move with velocities varying from one-third to almost equal that of light. These rays appear to be identical with the cathode rays of a high vacuum tube. The very small particles which constitute these rays are called electrons.

The gamma rays are very penetrating and will pass readily through bodies which will stop the other forms of radiations. They are produced in much smaller amounts than the other rays. They are not deflected by magnetic or electrostatic fields and seem to be identical with X-rays, that is they are light of exceedingly short wave length, very much shorter than that which is visible. They are probably produced by the impact of the beta rays.

Certain experiments have been performed with the  $\alpha$ -rays which furnish the strongest evidence yet brought forward that particles of about the calculated size of the atoms really exist. These experiments may be outlined as follows: A source of  $\alpha$ -rays is placed at some distance from and in line with a brass tube. In the axis of the tube and insulated from it is a wire connected with an electrometer. There is a high difference of potential between the tube and the wire. As the  $\alpha$ -rays enter the tube, they render the air within it a conductor and the needle of the electrometer moves. If the radioactive substance is far enough from the tube, the movement of the electrometer is intermittent and the jumps come at intervals of a few seconds. This shows that the stream of  $\alpha$ -particles is not continuous, or the movement would have been steady. By counting the jumps it is possible to determine the number of particles entering the tube in unit time. If now an insulated plate of metal the size of the opening in the tube be placed at the mouth of the latter, it will absorb the  $\alpha$ -rays and take up the charge of electricity that they carry. By determining the charge acquired in unit time, the charge on one particle can be calculated, and from this, assuming that the  $\alpha$ -particles are helium atoms, since 4 gram. of  $\alpha$ -particles carry  $2 \times 96,500$  coulombs, the number of particles in a gram mole of helium and the mass of a single molecule may be calculated. The results are that a gram mole contains  $6.1 \times 10^{23}$  molecules, and a molecule or atom, for they are identical in helium, weighs  $6.5 \times 10^{-24}$  gram.

A great deal of work has been done on radioactive substances with the result that the following facts seem to be established beyond a doubt. First, that the radioactive substances, uranium, thorium and radium are as truly elements for all chemical purposes as any others of our elements. Second, that these elements are continually and spontaneously undergoing transformations into other elements with a decrease in energy which appears in the form of heat and the various rays. One gram of radium gives out 118 grm. calories of heat per hour. Third, that in the case of radium, one of the products of the transformation is a gaseous substance, called radium emanation or niton, and that it is an element of the argon group of inert gases, since it is unattacked by any chemical treatment and has a characteristic spectrum similar to that of the other gases of the group. It has a molecular weight of 224, which is probably also its atomic weight. It is highly radioactive and changes in about a month into other elements, one of which is the undoubted element helium. Fourth, that radium is present in every uranium ore in practically a constant ratio to the uranium content of the ore. Fifth, that a substance having all the properties of lead with the exception of a slightly smaller atomic weight, 206 instead of 207.2, is a final product of the disintegration of uranium. These and other facts of a similar nature are interpreted to mean that radioactive elements decay and pass finally into other and more stable elements, and that they follow the law of successive reactions in going through a number of stages. Radium is one of the decomposition products of uranium, and the radium emanation in turn comes from the radium and goes on into helium, etc.

Some idea of the kind of evidence upon which these conclusions are based may be obtained from the following: Uranium salts which have been kept for some time give out all three kinds of rays. But when such a salt is dissolved in water and ammonium carbonate added until the precipitate which first forms is redissolved, a very small residue is left which gives no alpha rays but has all the beta and gamma activity of the original salt. The uranium carbonate which has redissolved has all the alpha activity of the original compound but gives rise to no beta or gamma rays. The undissolved precipitate is called uranium-X, and is chemically unlike uranium. If the uranium carbonate

be reconverted into the nitrate and then reprecipitated and dissolved by ammonium carbonate, no farther precipitate of uranium-X will be formed. But let both the uranium-X and the uranium preparation stand for some time, and it will be found that at the end of about 24 days the uranium-X will have lost half of its activity and the uranium will have regained half of the beta and gamma activity which it lost, and that these changes will go on until finally the uranium will recover its original activity. If now it be reprecipitated and redissolved by ammonium carbonate, a further residue of uranium-X will be obtained. This series of operations may be repeated as often as desired with the same sample of uranium, and it will always be found that when the repetition is made immediately that no further residue of uranium-X can be obtained, but after standing for some time it can always be secured. Therefore, uranium-X is something which grows in a uranium compound and which gives off beta and gamma rays and is half transformed into something else in 24 days, while uranium passes into uranium-X with the production of alpha rays. There is evidence that this uranium-X really consists of two substances uranium-X<sub>1</sub> and uranium-X<sub>2</sub>, and that X<sub>1</sub> changes into X<sub>2</sub> and the latter into uranium 2 which passes into a substance called ionium which goes into radium and this into radium emanation and so on as shown in the table on p. 499.

The following table represents the results of an immense amount of labor on the part of many investigators together with something of the theoretical explanation of the phenomena. While it contains a number of points which are still somewhat in question, it is, on the whole, worthy of confidence as a working theory and should be carefully studied. In the first column, is given the group and the sub-family in the periodic system of the element whose name begins the same horizontal line in the second column. The second column gives the equations representing the successive radioactive transformation of the element uranium. The figures just below the names of the elements are the rounded values for their atomic weights. The third column gives the rays produced, omitting the  $\gamma$  rays because these are produced by the  $\beta$  rays. In the last column, the average lives of the atoms of the radioactive elements are given.

Groups in periodic system	Theoretical Transformation Series		Rays	Average life
	Element transformed and atomic weights	Products and atomic weights		
6 Left	Uranium 1 238	= Uranium X <sub>1</sub> + Helium 234 4	$\alpha$	$8 \times 10^8$ years
4 Left	Uranium X <sub>1</sub> 234	= Uranium X <sub>2</sub> + Electron 234 $\frac{1}{1800}$	$\beta$	35.5 days
5 Left	Uranium X <sub>2</sub> 234	= Uranium 2 + Electron 234 $\frac{1}{1800}$	$\beta$	1.65 minutes
6 Left	Uranium 2 234	= Ionium + Helium 230 4	$\alpha$	$3 \times 10^8$ years
4 Left	Ionium 230	= Radium + Helium 226 4	$\alpha$	$2 \times 10^5$ years
2 Left	Radium 226	= Niton + Helium 222 4	$\alpha$	$2.44 \times 10^3$ years
0	Niton 222	= Radium A + Helium 218 4	$\alpha$	5.55 days
6 Right	Radium A 218	= Radium B + Helium 214 4	$\alpha$	4.3 minutes
4 Right	Radium B 214	= Radium C + Electron 214 $\frac{1}{1800}$	$\beta$	38.5 minutes
5 Right	Radium C 214	= Radium C' + Electron 214 $\frac{1}{1800}$	$\beta$	28.1 minutes
6 Right	Radium C' 214	= Radium D + Helium 210 4	$\alpha$	$10^{-6}$ seconds
4 Right	Radium D 210	= Radium E + Electron 210 $\frac{1}{1800}$	$\beta$	24 years
5 Right	Radium E 210	= Radium F + Electron 210 $\frac{1}{1800}$	$\beta$	7.2 days
6 Right	Radium F 210	= End (lead) + Helium 206 4	$\alpha$	196 days
4 Right	End lead 206			

For example, the table shows that uranium I, atomic weight 238, is a member of the left-hand family of group 6 in the periodic system, and that the theory says that an atom of uranium I spontaneously decomposes into an atom of uranium X<sub>1</sub>, atomic weight 234, and an  $\alpha$  particle which is, by theory, an atom of helium, atomic weight 4, carrying two charges of positive electricity.

According to this theory, the average life of the atom of uranium is  $8 \times 10^9$  years; but, just as many men live far beyond the average life of a man, so there will be uranium left in any given sample of the element long after it has been in existence  $8 \times 10^9$  years.

Uranium  $X_1$  belongs to group 4 two groups lower than uranium 1, and an inspection of the table will show that each transformation which produces  $\alpha$  rays gives a product which stands two groups lower in the periodic system with an atomic weight four units smaller than the parent element. A transformation which gives  $\beta$  rays yields a product standing one group higher than its parent, and having practically the same atomic weight because the mass of the  $\beta$  rays is so small that it may be neglected.

There are eight transformations yielding  $\alpha$  rays between uranium 1 and the final product. Since each of these lowers the atomic weight four units, the atomic weight of the end product should be  $238.2 - 8 \times 4 = 206.2$ .

Every uranium ore contains a substance which is precisely like lead in all its chemical and physical properties including the spectrum except that the atomic weight is smaller than that of ordinary lead, 206.4 in the purest ore, instead of 207.2 and its density is also slightly less. Thorium, atomic weight 232.4, undergoes six  $\alpha$ -ray transformations and therefore should yield a final product having an atomic weight of  $232.4 - 24 = 208.4$ . The thorium ores also contain a lead-like substance exactly like ordinary lead except that in this case the atomic weight is 208.4 instead of 207.2. These three kinds of lead differing only in their atomic weights are called isotopes, which may be defined as elements very similar in their chemical and physical properties, differing somewhat in atomic weight, but all occupying the same position in the periodic system. Radium B and radium D are also isotopes of lead. Uranium and uranium 2 are isotopes, and neon is now generally considered to be a mixture of isotopes of atomic weights 20 and 22.

The facts of radioactivity and the theoretical interpretation of them have led to the hypothesis that atoms are complex, consisting of a positively charged nucleus, which constitutes most of the mass of the atom, surrounded by negatively charged electrons, revolving in rings, sufficient in number to balance the

positive charge on the nucleus. The hydrogen atom is supposed to be the simplest of all and consists of a nucleus carrying one positive charge with one electron revolving around it.

The further hypothesis is now being made that the nucleus of an atom of any other element is made up by the combination of nuclei of hydrogen atoms and electrons, the latter not being sufficient in number to balance the positive charge on the hydrogen nuclei. For example, a helium atom is imagined as made up by the combination of four hydrogen nuclei and two electrons uniting to form a new nucleus carrying two positive charges around which two electrons carrying two negative charges revolve making an electrically neutral atom. In the case of the elements having a higher atomic weight than helium the nucleus is imagined to be made up of as many helium nuclei as there are multiples of 4 in the atomic weight plus enough hydrogen nuclei to complete the atomic weight. That is, the nitrogen nucleus is supposed to be made up of three helium nuclei, plus two hydrogen nuclei, plus one electron the whole nitrogen atom then would have seven electrons revolving around it. While all these speculations concerning the nature of atoms are very interesting, the student will of course recognize that they are very far from being established facts.

The number of electrons revolving around the nucleus of an atom is the same as what is called the atomic number of that element; *i.e.*, the atomic number of hydrogen is 1; of helium, 2; of lithium, 3; of nitrogen, 7, and so on. A periodic system can be prepared using the atomic numbers of the elements instead of their atomic weights as the basis of the arrangement. In this case it is noteworthy that no exceptions such as were made with argon and potassium, or tellurium and iodine are necessary to bring the elements into their proper relations. Hence the atomic numbers are apparently more closely related to the properties of the elements than are the atomic weights. Isotopes have the same atomic number.



## INDEX

- Absolute temperature**, 21  
    zero, 21
- Acetone**, 249
- Acetylene**, 248
- Acid**, acetic, 228, 245  
    alpha stannic, 413  
    antimonic, 438  
    antimonous, 436  
    arsenic, 433  
    arsenious, 431  
    boracic, 260  
    boric, 260  
    bromic, 147  
    carbolic, 242, 247  
    carbonic, 231  
    chloric, 136  
    chlorous, 141  
    chlorplatinic, 493  
    chlorplatinous, 493  
    chromic, 448  
    cyanic, 237  
    definition of, 105, 116  
    formic, 245  
    hydrazoic, 199  
    hydrobromic, 147  
    hydrochloric, 98  
        constant boiling, 103  
    hydrocyanic, 236  
        action upon catalyzers, 237  
    hydrofluoric, 155  
    hydrofluosilicic, 258  
    hydroiodic, 152  
    hydronitric, 199  
    hypobromous, 147, 148  
    hypochlorous, 123, 131  
        bleaching action of, 132  
        properties, 132  
    hyponitrous, 211  
    hypophosphoric, 221  
    hypophosphorous, 221  
    hyposulfurous, 182
- Acid, iodic, 153  
    manganic, 460  
    metaphosphoric, 221, 222  
    molybdic, 451  
    nitric, 204  
    nitrous, 210  
    nitrosylsulfuric, 176  
    orthophosphoric, 221  
    perchloric, 139  
        constant boiling, 139  
    perchromic, 450  
    periodic, 153  
    permanganic, 460, 463  
    persulfuric, 181  
    phosphomolybdic, 452  
    phosphoric, 221  
    phosphorous, 221, 223  
    picric acid, 247, 304  
    pyrophosphoric, 221, 222  
    selenic, 189  
    selenious, 188  
    silicic, 256  
    stannic, alpha, 413  
        beta, 413  
    sulfuric, 174  
        applications of, 180  
        aqueous, 180  
        concentration of, 179  
        contact process, 174  
        dissociation of, 180  
        identification of, 181  
        lead chamber process, 176  
        reactions for the preparation  
            of, 174, 175, 176, 177  
    sulfurous, 172  
        action on organisms, 173  
        bleaching action, 173  
        reducing action of, 172  
    telluric, 189  
    tellurous, 189  
    thioantimonic, 438

- Acid, thioantimonious, 438  
    thioarsenic, 432  
    thioarsenous, 432  
    thiostannic, 415  
    thiosulfuric, 182  
    tungstic, 454
- Acids, 105, 108  
    action of, 117  
    dibasic, 168  
    general methods for the preparation, 102, 136  
    of carbon, 245  
    of phosphorus, 221  
    strength of, 120
- Adsorption, 228
- Affinity, chemical, 43
- Air, 15, 199  
    a mixture, 202  
    and life, 203  
    composition of, 199  
    carbon dioxide in, 199  
    constituents of, 199  
    density of, 200  
    humidity of, 55  
    liquid, 200  
        experiments, 202  
        process of liquefying, 200
- Alcohol, denatured, 244  
    ethyl, 243  
    methyl, 228, 243  
    wood, 228, 243
- Alcohols, 243
- Aldehydes, 244
- Alkali metals, 275
- Alkaline earth metals, 316  
    general relationships, 316
- Allotropic modifications of sulfur, 162, 163
- Allotropy, 31
- Alloys, 268  
    acid resisting, 445
- Alpha rays, 495, 496, 498, 499
- Alum, 303, 399
- Alumina, 397
- Aluminates, 398
- Aluminothermy, 397
- Aluminum, 392, 393  
    acetate, 400
- Aluminum, amalgam, 395  
    carbide, 240  
    chemical properties of, 395  
    chloride, 398  
    hydroxide, 397  
    occurrence, 394  
    oxide, 397  
    physical properties of, 395  
    preparation of the metal, 394  
    silicate, 399, 400  
    subgroup, 392, 393  
    sulfate, 398  
    sulfide, 397, 400
- Alundum, 397
- Amalgams, 268, 354
- Ammonia, 193  
    action of chlorine on, 198  
    action of hypochlorites on, 198  
    chemical properties of, 196  
    combination of, with acids, 197  
    combustion of, 196  
    commercial source of, 194  
    drying of, 194  
    liquid, 195  
        as solvent, 195  
    occurrence of, 193  
    physical properties of, 195  
    preparation of, 194  
    salts of, 197  
    solubility of, 195  
    tests for, 198  
    use of, in manufacture of ice, 195
- Ammonium, 310  
    amalgam, 314  
    analytical reactions, 313  
    bicarbonate, 312  
    carbamate, 313  
    carbonate, 312  
    chloride, 194, 197, 310, 311  
    chlorplatinate, 313, 493  
    cobaltinitrite, 313  
    ferric citrate, 482  
    hydrotartrate, 313  
    hydroxide, 197, 311  
    iron alum, 480  
    molybdate, 451  
    nitrate, 197, 311

- Ammonium nitrate, decomposition**  
    of, 197  
    nitrite, 191  
        decomposition of, 191  
    oxalate, 313  
    oxide, 197  
    persulfate, 182  
    phosphomolybdate, 452  
    salts, 197, 310  
    sulfate, 311  
    sulfides, 312  
    thioarsenate, 432  
    thioarsenite, 432  
    thiocyanate, 313
- Amorphous substance, 50**
- Ampere, 119**
- Amygdalin, 237**
- Aniline, 242**
- Analysis, 64**
- Anglesite, 416**
- Anhydride, 132**  
    boric, 260  
    chromic, 448  
    hypochlorous, 132  
    hyponitrous, 211  
    iodic, 153  
    manganic, 460  
    nitric, 207  
    nitrous, 211  
    perchloric, 140  
    phosphoric, 221  
    phosphorous, 221  
    sulfuric, 173  
        action on water, 174  
    sulfurous, 170
- Anhydrite, 324**
- Anion, 112**
- Anode, 112, 113**
- Antichlor, 173, 182**
- Antimony, 434**  
    halogen compounds, 436  
    hydride, 435  
    hydroxide, 436  
    modifications, 435  
    nitrate, 437  
    occurrence of, 434  
    pentachloride, 438
- Antimony, pentasulfide, 438**  
    preparation, 434  
    properties of, 435  
    tetroxide, 439  
    tribromide, 437  
    trichloride, 436  
    trifluoride, 437  
    triiodide, 437  
    trioxide, 436  
    trisulfide, 434, 437  
    sulfate, 437
- Antimonyl, 436**
- Apatite, 214, 325**
- Aqua fortis, 206**  
    regia, 206
- Aquamarine, 337**
- Aragonite, 320**
- Argentite, 378**
- Argon, 263, 265**  
    group, 263
- Arsenic, 427**  
    diiodide, 434  
    disulfide, 434  
    family, 427  
        comparison, 442  
    halogen compounds, 431  
    modifications of, 428  
    occurrence of, 427  
    pentasulfide, 434  
    pentoxide, 433  
    preparation of, 428  
    properties of, 428  
    subgroup, 426  
    tribromide, 431  
    trichloride, 431  
    trifluoride, 431  
    trioxide, 430  
    trisulfide, 431  
    trivalent compounds, 429
- Arsenites, 431**
- Arsine, 429**
- Asbestos, 338**
- Assaying, 391**
- Atomic number, 501**  
    theory, 72  
    weights, standards of, 76  
    table of, 79

Azurite, 362, 371

## B

Babbitt metal, 418

Baking powder, 308, 399

Baking soda, 286

Barium, 316, 331

analytical properties of, 334

carbonate, 333

chlorate, 136, 334

chloride, 333

chromate, 334

dioxide, 332

hydroxide, 332

nitrate, 334

occurrence, 332

oxide, 332

platinocyanide, 493

properties of, 331

sulfate, 333

sulfide, 333

Barytes, 332

Base, 116

bullion, 417

Bases, 106

Bauxite, 394

Benzene, 242

Benzine, 239

Beryl, 337

Beryllium, 337

compounds, 337, 338

preparation, 337

properties of, 337

Bessemer converter, 471

process, 471

Beta rays, 495, 496, 498

Bischofite, 341

Bismuth, 439

dibromide, 441

dichloride, 441

hydroxide, 440

monosulfide, 441

monoxide, 441

nitrate, 440

occurrence of, 439

oxychloride, 441

Bismuth, preparation of, 439

properties of, 440

salts, 440

subnitrate, 441

sulfate, 439

sulfide, 441

tetroxide, 441

tribromide, 441

trichloride, 441

triiodide, 441

trioxide, 440

Blast furnace, copper, 362

iron, 467

lead, 416

Bleaching, powder, 93, 128, 132, 323

with chlorine, 96, 133

with hydrogen peroxide, 86

with sulfur dioxide, 173

Blende, 345, 350

Blue print paper, 482

Blue vitriol, 370

Body, properties of, 1

Bog ore, 466

Boiling point, 54

Bone black, 228

Borax, 261, 291

Bordeaux mixture, 370

Bornite, 362

Boron, 260

halogen compounds of, 261

nitride, 262

trioxide, 260

Brass, 348, 366

Braunite, 457

Brick, 402

Britannia metal, 418

British thermal unit, 51

Bromine, 142

chemical properties, 145

hydrate, 145

occurrence, 142

oxygen compounds, 147

physical properties, 144

preparation, 143

Bronze, 366

Brownian movement, 433

B.t.u., 51

**Burette**, 108

**C**

**Cadmium**, 316, 337, 351

analytical properties, 352

compounds, 352

occurrence, 351

preparation of, 351

properties of, 351

sulfide, 352

yellow, 352

**Calamine**, 345

**Calaverite**, 386

**Calcite**, 320

**Calcium**, 316

acid sulfite, 246

analytical properties of, 330

arsenide, 429

bicarbonate, 320

borate, 261

bromide, 323

carbide, 248, 327

carbonate, 320

decomposition of, 321

chlorate, 134

chloride, 322

cyanamide, 193, 327

ferrite, 479

fluoride, 323

hydride, 317

hydroxide, 319

hypochlorite, 323

iodide, 323

manganite, 459

nitrate, 323

occurrence, 316

oxalate, 327

oxide, 317

phosphate, 325

phosphide, 217

preparation of, 317

properties of, 317

silicate, 328

sulfate, 324

sulfide, 325

**Calomel**, 355

**Caloric**, 51

**Carbohydrates**, 243, 246

**Carbon**, 225

allotropic forms of, 225, 229

amorphous, 227

circulation of, 232

compounds, types of, 242

dioxide, 14, 230

in air, 199

occurrence of, 230

liquid, 230

preparation of, 231

properties of, 230

solid, 230

solution of, 231

test for, 231, 232

disulfide, 235

monoxide, 234

properties of, 235

formation of, 234, 250

nitrogen compounds of, 236

occurrence of, 225

oxygen compounds of, 230

soot, 228

tetrachloride, 241

**Carborundum**, 259

**Carnalite**, 297, 341

**Cassiterite**, 409

**Catalysis**, 44

**Catalytic action**, 46

**Catalyzer**, 46

**Cathode**, 111, 113

**Cation**, 112, 113

**Caustic potash**, 14, 297

**Celestite**, 331

**Cell**, dry, 311, 459

Daniell, 374

Leclanche, 459

sal ammoniac, 311, 459

storage, lead, 424

Edison, 489

**Cellulose**, 246

**Cement plaster**, 324

Portland, 403

**Cementite**, 476

**Cements**, 403

**Centigrade**, 21

**Cerite**, 408

**Cerium**, 408

- Cerussite, 416
- Cesium, 275, 309
- Chalcocite, 362
- Chalcopyrite, 362
- Chalk, 320
- Changes, 2
  - chemical, 2
  - physical, 2
- Charcoal, 225, 228
- Chemical heat effects, 90
- Chemistry, definition of, 1
  - organic, 225
- Chile salt-peter, 204, 286
- China clay, 401
- Chlorates, 134, 135
  - properties of, 135
- Chloride of lime, 128, 323
- Chlorides, naming of, 97
- Chlorine, 92
  - acids, 122
  - and hydrogen compounds, 99
  - as ion, 113, 114
  - bleaching action of, 96, 133
  - combustion in, 96
  - combination with hydrogen in sunlight, 99
  - dioxide, 122, 140
  - electrolytic preparation, 95
  - hydrate, 97
  - liquid, 96
  - monoxide, 122, 132, 133
  - occurrence, 92
  - oxyacids, 122
  - oxygen compounds, 122
  - oxides, 122
  - preparation, 92, 95
  - properties, chemical, 96
    - physical, 95
  - reaction with methane, 100, 241
  - water, 96
    - decomposition in sunlight, 96
- Chlorites, 140
- Chloroform, 241
- Chlorplatينات, 493
- Choke-damp, 240
- Chromates, 448
- Chrome alum, 447
  - iron, 444
- Chrome steel, 444
  - yellow, 423, 448
- Chromic compounds, 446
  - chloride, 447
  - hydroxide, 446
  - oxide, 446
  - sulfate, 447
- Chromium, 443, 444
  - analytical reactions, 450
  - occurrence, 444
  - passivity, 445
  - photochemical reactions of, 450
  - preparation of, 444
  - properties, 444
  - subgroup, 443
- Chromous acetate, 445
  - compounds, 445
- Chromyl chloride, 449
- Cinnabar, 353, 358
- Clay, 400
- Coal, 229
- Cobalt, 465, 484
  - alums, 486
  - chloride, 485
  - complex cyanides of, 486
  - glass, 486
  - nitrate, 486
  - occurrence, 484
  - properties of, 485
  - sulfate, 485
  - sulfide, 486
  - trioxide, 486
- Cobaltic alums, 486
  - ammonia compounds, 487
  - compounds, 486
- Cobaltinitrites, 487
- Cobaltite, 484
- Coefficient of expansion, 20
- Coke, 229
- Colloidal solutions, 257, 433
- Columbium, 427
- Combination, 16
- Combining weights, 71
- Combustion, 13
  - rôle of the air in, 15
- Complex salts, definition of, 342
- Compounds, 28
  - Concentration, 44

- Conditions, standard, 18**  
**Conductivity, molecular, 119**  
**Conductors of first class, 110**  
     of second class, 110  
**Conservation of elements, 28**  
     of energy, 10  
     of mass, 11  
**Converter, Bessemer, 471**  
     copper, 363  
**Copper, 361**  
     action of nitric acid on, 205  
     alloys of, 366  
     analytical properties of, 373  
     arsenite, 431  
     chemical properties of, 365  
     converter, 363  
     electrolytic refining of, 364  
     family, general relations of, 361  
     ferrocyanide, 371  
     history of, 361  
     matte, 362  
     metallurgy of, 362  
     nitrate, 370  
     occurrence of, 361  
     physical properties of, 365  
     sulfate, 370  
**Copperas, 478**  
**Corrosive sublimate, 356**  
**Corundum, 397**  
**Coulomb, 112, 375**  
**Cream of Tartar, 436**  
**Critical pressure, 25**  
     temperature, 25  
**Crucible steel, 474**  
**Cryolite, 394**  
**Crystallization, 137**  
**Crystals, 49**  
**Cupel, 391**  
**Cupric acetate, 371**  
     ammonia ion, 369  
     carbonate, 371  
     chloride, 369  
     compounds, 368  
     ferrocyanide 371  
     hydroxide, 369  
     ion, 368  
     nitrate, 370  
**Cupric oxide, 369**  
     sulfate, 370  
     sulfide, 371  
**Cuprite, 362**  
**Cuprous bromide, 367**  
     chloride, 367  
     compounds, 366  
     cyanide, 368  
     iodide, 367  
     oxide, 366  
     sulfide, 368  
**Cyanates, 237**  
**Cyanogen, 236**
- D
- Daniell cell, 374**  
**Davy, 92, 277, 296**  
**Deacon's process, 93**  
**Decomposition, 16**  
**Deliquescent, 63**  
**Density, 11**  
     of gases, 18  
**Diamond, 226**  
**Diamonds, artificial preparation, 226**  
**Dibasic acids, 168**  
     dissociation, 168  
**Dichromates, 448**  
**Diffusion, 36**  
**Disinfectant action of chlorine, 96**  
     of hydrogen peroxide, 85  
**Dissociation, degree of, 118, 120**  
**Distillation, 47, 85**  
**Distribution, law of, 150**  
**Dolomite, 338, 341**  
**Double salt, definition of, 342**  
**Dyes, 242**  
**Dynamite, 247**  
**Dyne, 9**
- E
- Earth's crust, composition of, 274**  
**Earthen-ware, 402**  
**Efflorescent, 64**  
**Electric furnace, 215, 227, 236, 259, 327**  
**Electrode, 111**

Electrolysis, 112  
 Electrolytes, 110  
 Electrolytic dissociation, 113  
 Electromotive force, 376  
 Electron, 496, 500  
 Electroplating, cobalt, 485  
     gold, 390  
     nickel, 488  
     silver, 383  
 Elements, 28  
     definition of, 28  
     metallic, 267  
     table of, 79  
 Emerald, 337  
 Emery, 397  
 Energy, 10  
     conservation of, 10  
     free, 374  
 Enzymes, 243  
 Epsom salts, 342  
 Epsomite, 342  
 Equations, 81  
 Equilibrium, 44  
     constant, 126  
     mobile, 57  
 Equivalent weight, 160  
 Erg, 10  
 Esters, 243, 246  
 Ethane, 241  
 Ethers, 246  
 Ethyl acetate, 246  
     alcohol, 243  
     chloride, 242  
 Ethylene, 247  
 Expansion, coefficient of, 20  
 Explosives, 89, 247

## F

Fact, relation to theory, 75  
 Fehling's solution, 369  
 Feldspar, 401  
 Ferrates, 483  
 Ferric alums, 480  
     chloride, 480  
     compounds, 478  
     reduction of, 479  
     ferrocyanide, 481  
     hydroxide, 479

Ferric oxalate, 282  
     oxide, 479  
     phosphate, 481  
     sulfate, 480  
     sulfide, 480  
     thiocyanate, 480  
 Ferricyanides, 481  
 Ferrites, 479  
 Ferrocyanides, 481  
 Ferromanganese, 457, 474  
 Ferrous bromide, 478  
     carbonate, 478  
     chloride, 478  
     compounds, 477  
     ferricyanide, 482  
     ferrite, 479  
     hydroxide, 477  
     iodide, 478  
     oxalate, 482  
     oxide, 477  
     sulfate, 477  
     sulfide, 478  
 Fertilizers, 210, 213, 222, 326, 327  
 Fire assaying, 391  
 Fire-damp, 240  
 Flames, 251  
 Flint, 256  
 Flotation, 345  
 Fluorescence, 455  
 Fluorine, 142, 182  
     occurrence, 154  
     preparation of, 154  
     properties of, 154  
 Fluorspar, 154  
 Fool's gold, 481  
 Force, 9  
 Formaldehyde, 244  
 Formaline, 245  
 Formulas, 78  
 Franklinite, 345  
 Free energy, 374  
 Freezing-point, 60  
     abnormal lowering of, 109  
     lowering of solvent, 60  
 Fusion, heat of, 50

## G

Galena, 416

**Iallium**, 392, 405  
**Iamma rays**, 495  
**Iarnet**, 394  
**Gas**, Blau, 251  
    coal, 249  
    drying of, 35  
    mantles, 409  
    natural, 240  
    producer, 250  
    water, 250  
**Gaseous state**, 7  
**Gases**, density, 18  
    fuel, 249  
    molar weight of, 68  
**Gasoline**, 239  
**Gay Lussac tower**, 177  
**Genthite**, 487  
**German silver**, 488  
**Germanium**, 407, 409  
    subgroup, 407, 409  
**Glass**, 328  
    etching, 156  
**Glover's tower**, 177  
**Glucinum**, 337  
**Glucose**, 246, 247  
**Gold**, 361, 386  
    analytical properties of, 391  
    and silver, parting of, 387  
    chemical properties, 389  
    complex cyanides, 390  
    general relationships, 361  
    halogen compounds of, 389  
    hydroxides, 389  
    metallurgy of, 387  
        amalgamation, 387  
        chlorination, 387  
        cyanide, 387  
        smelting, 387  
    occurrence of, 386  
    oxides, 389  
    physical properties of, 388  
    sulfides, 390  
**Goldschmidt process**, 396  
**Gram**, 9  
    ion, 113  
    mole, 69  
    volume of gas, 69  
**Granite**, 257

**Graphite**, 226  
**Green vitriol**, 478  
**Greenockite**, 352  
**Gun cotton**, 247  
    powder, 247, 300  
**Gypsum**, 324

## H

**Halogen subgroup**, 456  
**Halogens**, 142  
**Hard water**, 321  
**Hausmanite**, 457  
**Heat measurement**, 51  
    of formation, 90  
    of fusion, 50  
    of neutralization, 116  
    of vaporization, 56  
    units of, 51  
**High speed steel**, 453  
**Helium**, 200, 263, 264, 495, 497, 499  
**Hematite**, 466  
**Homologous series**, 237  
**Humidity, relative**, 55  
**Hydrargillite**, 397  
**Hydrates**, 62  
**Hydraulic mortar**, 403  
**Hydrazine**, 198  
**Hydrocarbons**, 237, 242  
    cracking, 240  
    paraffin series, 237  
    unsaturated, 247  
**Hydrogen**, 32  
    absorption by metals, 39  
    and the gas laws, 38  
    as ion, 114  
    bromide, 145  
        properties of, 146  
    chloride, 92, 98  
        hydrates, 103  
        liquid, 102  
    preparation, 98, 99, 100  
    properties, 102  
    solubility, 102  
    combustion in chlorine, 98  
    fluoride, 155  
        physical properties, 155  
    iodide, 151

- Hydrogen iodide, chemical properties, 152  
     physical properties, 152  
 liquid, 39  
 occurrence, 32  
 peroxide, 84  
     composition, 88  
     explosive properties, 89  
     heat of formation, 90  
     molecular weight, 86  
     oxidizing action, 86  
     preparation, 84, 88  
     properties, 84  
     reducing action, 86  
 phosphide, liquid, 217, 219  
     solid, 217, 219  
 preparation, 32—35  
 properties, chemical, 40  
     physical, 36  
 purification, 35  
 selenide, 188  
 solid, 39  
 spectrum, 39  
 sulfide, 166  
     analytical reactions of, 169  
     chemical properties, 167  
     physical properties, 167  
     preparation, 166  
     reducing agent, 169  
     solution in water, 168  
 telluride, 189  
 Hydrolysis, 157  
 Hypo, 182  
 Hypochlorites, bleaching action, 129  
     decomposition of, 129  
 Hyponitrites, 211
- I
- Ice, 49  
     heat of fusion, 50  
     manufacture of, 195  
     properties of, 49  
 Iceland spar, 320  
 Ilmenite, 408  
 Indium, 392, 405  
 Invar, 488  
 Iodine, 148  
     chemical properties, 150  
     oxides of, 153  
     oxygen compounds of, 152  
     pentoxide, 153  
     physical properties, 149  
     preparation, 148  
 Ion, actual, 119  
     potential, 119  
 Ionium, 499  
 Ionization, degree of, 118, 120  
 Ions, 112, 113, 115  
 Iridium, 465, 491, 492  
 Iron, 466  
     alums, 480  
     analytical properties, 484  
     blast furnace, 467  
     reactions in, 469  
     Bessemer process, 471  
     cast, 467, 470  
     chemical properties, 476  
     corrosion of, 483  
     cyanogen compounds, of, 481  
     dialyzed, 479  
     family, 465  
     galvanized, 348  
     general relationships of, 466  
     metallurgy of, 467  
     occurrence, 466  
     ore, mining, 467  
     spathic, 466  
     ores, 466  
     passivity, 477  
     physical properties of, 476  
     pig, 468  
     puddling process for, 475  
     salts of. (See *Ferrous* and *Ferric*.)  
     subgroup, 465  
     wrought, 470, 475  
 Isotopes, 500
- J
- Jasper, 256  
 Joule, 10, 51
- K
- Kainite, 297  
 Kaolin, 401

Kerosene, 239  
 Kidney ore, 466  
 Kieserite, 342  
 Kilojoule, 10  
 Krypton, 200, 263, 265

## L

Lakes, 400  
 Lampblack, 228  
 Lanthanum, 392, 393  
 Lapis lazuli, 496  
 Law, Boyle's, 19  
     Charles', 20  
     combining volumes of gases, 67  
         weights, 71, 72  
     conservation of elements, 28  
     constant proportions, 27  
     Dalton's, 37  
     definite proportions, 27  
     diffusion of gases, 38  
     distribution, 150  
     Dulong and Petit's, 77  
     Faraday's, 112  
     fundamental, 4  
     Gay Lussac's and Dalton's, 20,  
         22  
     gravitation, 3  
     Henry's, 102  
     Mass action, 123-125  
     mobile equilibrium, 57  
     multiple proportions, 84  
     natural, 3  
     partial pressure, 37  
     solubility of gases, 102  
     successive reactions, 131  
 Laws, gas, 18  
     combined gas, 23  
 Lead, 225, 415  
     acetate, 420  
     basic, 421  
     alloys, 418  
     analytical properties of, 425  
     arsenate, 434  
     carbonate, 421  
     chemical relationships, 415  
     chloride, 420  
     chromate, 423

Lead dioxide, 419, 420  
     hydroxide, 419  
     metallurgy of, 416  
     nitrate, 420  
     occurrence, 416  
     oxides of, 419  
     physical and chemical proper-  
         ties of, 418  
     poisonous action of, 418  
     purification of, 417  
     sulfate, 423  
     sulfide, 424  
 LeBlanc process, 282  
 Length, 9  
 Lepidolite, 314  
 Lignin, 246  
 Lime, 317  
     kiln, 318  
     milk of, 319  
     slaked, 319  
     water, 232, 319  
 Limestone, 320  
 Limonite, 466  
 Linen, 246  
 Liquid state, 7  
 Litharge, 419  
 Lithium, 275, 314  
     analytical properties, 315  
     carbonate, 315  
     chloride, 315  
 Lithophone, 350  
 Lithosphere, composition of, 274  
 London purple, 431

## M

Magnalium, 395  
 Magnesia, 339  
 Magnesite, 338, 341  
 Magnesium, 337, 338  
     alloys, 339  
     ammonium phosphate, 343  
     analytical reactions, 343  
     carbonate, 341  
     chloride, 341  
     ferrite, 479  
     hydroxide, 339  
     solution of, in ammonium  
         salts, 320

- Magnesium nitride**, 343  
    occurrence of, 338  
    oxide, 339  
    phosphates, 343  
    preparation of, 338  
    properties of, 338  
    subgroup, 337  
        general relations of, 337  
    sulfide, 343  
    sulfate, 342
- Magnetite**, 466
- Manganates**, 460
- Manganese**, 456  
    alloys, 457  
    alums, 459  
    analytical properties, 464  
    blende, 457  
    bronze, 457  
    dioxide, 459  
    general relations of, 456  
    heptavalent, 460  
    heptoxide, 464  
    hexavalent, 460  
    occurrence of, 456  
    preparation of, 457  
    properties of, 457  
    spar, 457  
    tetrachloride, 459  
    tetrahydroxide, 459  
    tetravalent compounds of, 459  
    trioxide, 460  
    trivalent, 458  
    valences of, 456
- Manganic salts**, 458
- Manganite**, 457
- Manganites**, 459
- Manganous ammonium phosphate**, 458  
    borate, 458  
    carbonate, 458  
    compounds, 457  
    hydroxide, 457  
    sulfate, 458  
    sulfide, 458
- Malachite**, 362, 371
- Marble**, 320
- Marl**, 401
- Marsh gas**, 237, 240
- Marsh's test**, 430
- Mass**, 9  
    conservation of, 11  
    action, law of, 125, 126
- Matches**, 224
- Meerschaum**, 318
- Mendeljeff**, 270
- Mercuric ammonia**, 359  
    bromide, 357  
    chloride, 356  
    compounds, 356  
    cyanide, 358  
    iodide, 357  
    nitrate, 358  
    oxide, 12, 356  
    sulfate, 358  
    sulfide, 358
- Mercurous bromide**, 355  
    chloride, 355  
    compounds, 355  
    iodide, 355  
    nitrate, 355  
    oxide, 355  
    sulfate, 356  
    sulfide, 356
- Mercury**, 316, 337, 353  
    analytical properties of, 360  
    chemical properties of, 354  
    complex compounds of, 359  
    fulminate, 359  
    occurrence of, 353  
    physical properties of, 353  
    preparation of, 353
- Metals**, action of nitric acid on, 205  
    chemical properties of, 268  
    classification of, 268  
    conductivity of, for heat, 267  
    electrical conductivity of, 267  
    physical properties of, 267  
    the earth, 392
- Methane**, 237, 240  
    preparation of, 240
- Methyl chloride**, 241  
    ether, 242
- Methylene**, 247  
    chloride, 241
- Mica**, 394
- Minium**, 419

**Mirrors**, 385  
**Mixtures**, constant boiling, 103  
    mechanical, 8  
**Molar weight**, 68  
**Molecular conductivity**, 119  
    theory, 74  
    weight, 75  
        determination, 86  
        of gases, 68  
**Molybdenite**, 451  
**Molybdenum**, 443, 451  
    oxides of, 451  
    properties of, 451  
**Monel metal**, 488  
**Monozite**, 392  
**Mordants**, 400  
**Mortar**, 320

## N

**Naphtha**, 239  
**Natural cements**, 403  
**Neodymium**, 426, 427  
**Neon**, 200, 263, 264  
**Nessler reagent**, 357  
**Neutralization**, 106, 116  
    heat of, 116  
    reacting ratio, 107  
**Nickel**, 465, 487  
    ammonia ions, 489  
    ammonium sulfate, 488  
    carbonyl, 490  
    chloride, 489  
    compounds, 488  
    cyanide, 489  
    dimethyl glyoxime, 490  
    glance, 487  
    hydroxides, 489  
    occurrence of, 487  
    oxides, 489  
    plating, 488  
    properties of, 488  
    steel, 488  
    sulfate, 489  
    sulfide, 489  
**Nicollite**, 487  
**Niton**, 263, 265, 497, 499

**Nitrogen and life**, 212  
**Nitric oxide**, 192  
    preparation of, 207  
    properties of, 207  
**Nitrides**, 192  
**Nitrites**, 210  
**Nitro-benzene**, 207  
**Nitro-compounds**, 207  
**Nitrogen**, 191  
    chemical properties, 192  
    hydrogen compounds of, 192  
    occurrence of, 191  
    oxides, 203  
    oxyacids of, 203  
    pentoxide, 207  
    peroxide, 192, 208  
        preparation of, 209  
    physical properties of, 191  
    preparation of, 191  
    trioxide, 211  
**Nitroglycerine**, 207, 247  
**Nitrous anhydride**, preparation of,  
    211  
    oxide, 211  
**Nomenclature of acids and salts**, 122  
**Normal solution**, 107, 108  
**Nucleus**, 500  
**Number, atomic**, 501

## O

**Ocean**, composition of, 274  
**Ocher**, 401  
**Olivine**, 338  
**Onnes**, 264  
**Opal**, 256  
**Open hearth furnace**, 473  
    process, 473  
**Orpiment**, 427, 431  
**Osmium**, 465, 491  
**Osmotic pressure**, 371  
**Oxidation**, 185  
    definition of, 186  
    slow, 27  
    types of changes considered, 185  
**Oxides**, 29  
    naming of, 98

Oxy-hydrogen blowpipe, 42

Oxygen, 12

density of, 18, 23

discovery of, 12

formation from chlorine and  
sodium hydroxide, 129

liquid, 24

occurrence, 29

preparation of, 16

properties, chemical, 18, 25

physical, 18, 24

solid, 25

subgroup, 443

Ozone, 29

chemical properties, 30

physical properties, 29

preparation of, 29

uses, 30

## P

Painter's colic, 418

Palladium, 465, 491, 492

Paraffin, 239

series, 237

Paris green, 431

Parke's process, 379

Partial pressure, 37

Pearlash, 301

Perchlorates, 139

Perchloric anhydride, 140

Periodates, 153

Periodic system, 269

table of, 271

Permanent hardness, 321

Permanganates, 460

"Permutite," 345

Petalite, 314

Petroleum, crude, 238

Pewter, 418

Phosphate fertilizer, 222, 326

Phosphates, 222

Phosphine, 217

properties of, 218

Phosphonium bromide, 219

chloride, 219

iodide, 218

Phosphorus, 214

acids, 221

allotropic modifications, 215

applications of, 224

halogen compounds of, 219

hydrogen compounds of, 217

luminosity of, 216

occurrence of, 214

ordinary, 215

oxygen compounds of, 220

pentachloride, 220

pentoxide, 220

preparation of, 215

red, 217

sulfides, 223

trichloride, 219

trioxide, 220

Photochemical action, 97, 99, 233

Photography, 384

Physical state, 7

Pink salt, 414

Pitchblende, 454

Plaster of Paris, 324

Platinates, 493

Platinic compounds, 493

hydroxide, 493

sulfide, 494

Platino cyanides, 493

Platinous compounds, 493

hydroxide, 493

sulfide, 494

Platinum, 465, 490, 491, 492

catalytic agent, 45, 173, 175, 492

black, 492

metals, 490

table for comparison of, 491

sponge, 493

subgroup, 465

ware, care of, 492

Plumbites, 419

Polysulfides, 170

Porcelain, 401

Portland cement, 403

Potash, 301

caustic, 297

Potassium, 275, 294

adsorption of, by soils, 294

Plum 202, 200

**Potassium, aluminate, 398**  
**amalgam, 296**  
**analytical properties of, 303**  
**antimony tartrate, 436**  
**bicarbonate, 301**  
**bromate, 298**  
**bromide, 298**  
**carbonate, 301**  
**chemical properties of, 296**  
**chlorate, 17, 93, 134, 137, 298**  
**chloride, 17, 297**  
**chlorplatinat, 304, 493**  
**chlorplatinite, 493**  
**chromate, 448**  
**chrome alum, 447**  
**cobalticyanide, 486**  
**cobaltinitrite, 303**  
**compounds and plants, 295**  
**cyanate, 302**  
**cyanide, 301**  
**fertilizers, 296**  
**ferricyanide, 482**  
**ferrocyanide, 302, 481**  
**ferrous ferrocyanide, 481**  
**fluoride, 155**  
**fluosilicate, 304**  
**history of, 296**  
**hydride, 297**  
**hydrogentartrate, 304**  
     **changes in the solubility, 304**  
     **theory of, 305**  
**hydroxide, 297**  
**iodide, 298**  
**manganate, 460**  
**metantimonate, 439**  
**nickel cyanide, 490**  
**nitrate, 299**  
**nitrite, 210**  
**occurrence of, 294**  
**oxides, 297**  
**perchlorate, 139, 299, 304**  
**permanganate, 93, 461**  
     **as oxidizing agent, 461**  
**persulfate, 182**  
**physical properties of, 296**  
**picrate, 304**  
**platinate, 493**  
**plumbate, 490**

**Potassium, preparation of, 296**  
     **pyroantimonate, 439**  
     **sulfate, 302**  
     **thioarsenate, 432**  
     **thioarsenite, 432**  
**Potential series, 376**  
**Potter's earth, 401**  
**Pottery, 401**  
**Pressure of atmosphere, 18, 25**  
     **critical, 25**  
     **effect of, on melting-point, 56**  
     **osmotic, 371**  
**Priestly, 12**  
**Propane, 238, 242**  
**Properties, definition of, 1**  
     **chemical, 5**  
     **physical, 5**  
**Proustite, 378**  
**Prussian blue, 481**  
**Pseudomorphs, 164**  
**Puddling furnace, 475**  
**Pyrargyrite, 378**  
**Pyrite, 466, 481**  
**Pyrolusite, 457**

## Q

**Quantitative relations, 27**  
**Quartz, 256**  
**Quicksilver, 353**

## R

**Radical, methyl, 241**  
     **ethyl, 241**  
     **propyl, 242**  
**Radioactive changes, table of, 499**  
**Radioactivity, 495**  
**Radium, 316, 335, 495**  
     **heat given out by, 497**  
     **emanation, 263, 265, 497, 499**  
     **properties of, 335**  
     **transformation into helium, 497**  
**Ramsay, 265, 266**  
**Rare earths, 392**  
**Rayleigh, 265**  
**Rays, Alpha, 495, 496**  
     Beta, 495, 496

Rays, Gamma, 495, 496, 498

Reactions, 14

reversible, 43

Reagent, 14

Realgar, 434

Recrystallization, 137

Red lead, 419

precipitate, 356

prussiate of potash, 482

Reduction, 185

definition of, 186

types of changes considered,  
186

Reversible reactions, 43

Rhodium, 465, 491, 492

Rouge, 479

Rubidium, 275, 309

Ruby, 397

Ruthenium, 465, 491

subgroup, 465

Rutile, 408

## S

Sal ammoniac, 311

Salt, 116, 278

cake, 283

-complex, 342

double, 342

Saltpeter, 204, 299

Salts, 108, 112

acid, 168

mono and di, 168

neutral, 168

primary, 168

properties, 108

secondary, 168

separation of, 137

solubility of, theory of change  
of, 305

Sapphire, 397

Saturated solution, 61

Scandium, 392

Scheele, 12

Scheele's green, 431

Schlippe's salt, 438

Schoenite, 302, 342

Scorifier, 391

Selenium, 187

chemical properties, 188

dioxide, 188

physical properties, 187

Semiporcelain, 402

Serpentine, 338

Sherardizing, 348

Siderite, 466

Siemens-Martin process, 473

Sienna, 401

Silica, 256

Silicates, 256

Silico-chloroform, 258

Silicon, 225, 255

carbide, 259

dioxide, 256

fluoride, 258

halogen compounds, 258

hydride, 257

preparation, 255

properties, 255

Silk, artificial, 369

Silver, 361, 378

analytical properties of, 385

arsenate, 384

arsenite, 384

carbonate, 384

chemical properties, 380

chlorate, 136

chlorplatinite, 493

chromate, 384

cyanide, 383

general relations of, 378

halides, 382

compounds with ammonia,  
382

metallurgy, 378

nitrate, 383

occurrence, 378

oxides, 381

properties, chemical, 380

physical, 380

sulfate, 383

sulfide, 384

thiocyanate, 384

Slaked lime, 319

Smalt, 486

Smaltite, 484

- Smithsonite**, 345  
**Soda ash**, 283  
**Sodium**, 275, 276  
     acetate, 292  
     aluminate, 398  
     amalgam, 280  
     amide, 197  
     ammonium phosphate, 223  
     analytical properties of, 293  
     arsenate, 434  
     arsenite, 431  
     bicarbonate, 277  
     bromide, 279  
     carbonate, 127, 232, 281  
         occurrence, 282  
         black ash, 283  
         preparation of, Le Blanc  
             process, 282  
             Solvay process, 284  
         properties of, 284  
         uses of, 286  
     chlorate, 130  
     chloride, 278  
     chlorite, 140  
     chromate, 448  
     cobaltinitrite, 303  
     cyanide, 292  
     disulfite, 289  
     ferrocyanide, 481  
     history, 277  
     hydride, 278  
     hydroxide, 280  
     hypochlorite, 127  
     hyponitrite, 211  
     hyposulfite, 182  
     iodide, 279  
     manganate, 460  
     metabisulfite, 289  
     metaphosphate, 223  
     monoxide, 279  
     nitrate, 277, 286  
     nitrite, 287  
     occurrence, 276  
     oxides, 279  
     perchlorates, 130  
     peroxides, 280  
     phosphates, 222, 290  
     sulfate, 287  
     sulfide, 289  
     sulfite, 289  
     tetraborate, 291  
     thioantimonate, 438  
     thioarsenate, 432  
     thioarsenite, 432  
     thiostannate, 413  
     thiosulfate, 290  
     tungstate, 453  
**Solder**, 418  
**Solid state**, 7  
**Solubility**, 7, 61  
     of salts, theory of change, 305  
**Solute**, 58  
**Solution**, 7, 57  
     normal ionic, 376  
     saturated, 61  
**Solutions**, 61  
     colloidal, 257, 433  
     normal, 107, 108  
**Solvay process**, 284  
**Solvent**, 58  
**Soot**, 228  
**Spathic iron ore**, 466  
**Specific gravity**, 11  
     heat, 51  
**Sphalerite**, 345  
**Spiegeleisen**, 457  
**Spinel**, 398  
**Stannates**, 413  
**Stannic chloride**, 414  
     hydroxide, 413  
     oxide, 413  
     sulfide, 414  
**Stannites**, 410  
**Stannous chloride**, 412  
     compounds, 412  
     hydroxide, 412  
     oxalate, 412  
     oxide, 412  
     nitrate, 412  
     sulfate, 412

Water, hard, 321  
  heat of vaporization, 56  
  molar weight of, 69  
  properties, chemical, 62  
    physical, 48  
  purification of, 48  
  softening, 344  
  super-cooled, 50  
  vapor, 52  
    pressure, 53  
Weight, 9  
  change in, 10  
  conservation of, 11  
Weights, equivalent, 160  
Welsbach mantles, 409  
White lead, 421  
Willimite, 345  
Witherite, 332  
Wolfram, 452  
Wood, petrified, 256  
  pulp, 246  
Work, 10  
  lead, 417  
Wrought iron, 470, 475  
Wulfenite, 451

## X

Xenon, 200, 263, 265

## Y

Yellow prussiate of potash, 481  
Yttrium, 392, 393

## Z

Zeolite, 345  
Zinc, 337, 345  
  alloys, 348  
  analytical properties, 351  
  blende, 345  
  carbonate, 350  
  chloride, 349  
  ferrite, 479  
  hydroxide, 348  
  metallurgy, 345  
  occurrence, 345  
  oxide, 348  
    in paint, 348  
  properties, 347  
  silicates, 345  
  spar, 345  
  sulfate, 350  
  sulfide, 350  
  vitriol, 350  
Zircon, 408  
Zirconium, 408

# INTERNATIONAL ATOMIC WEIGHTS, 1917

	Symbol	Combining weight		Symbol	Combining weight
Aluminum.....	Al	27.1	Molybdenum.....	Mo	96.0
Antimony.....	Sb	120.2	Neodymium.....	Nd	144.3
Argon.....	A	39.88	Neon.....	Ne	20.2
Arsenic.....	As	74.96	Nickel.....	Ni	58.68
Barium.....	Ba	137.37	Niton (radium emanation).	Nt	222.4
Bismuth.....	Bi	208.0	Nitrogen.....	N	14.01
Boron.....	B	11.0	Osmium.....	Os	190.9
Bromine.....	Br	79.92	Oxygen.....	O	16.00
Cadmium.....	Cd	112.40	Palladium.....	Pd	106.7
Calcium.....	Ca	40.07	Phosphorus.....	P	31.04
Carbon.....	C	12.005	Platinum.....	Pt	195.2
Cerium.....	Ce	140.25	Potassium.....	K	39.10
Cesium.....	Cs	132.81	Praseodymium.....	Pr	140.9
Chlorine.....	Cl	35.46	Radium.....	Ra	226.0
Chromium.....	Cr	52.0	Rhodium.....	Rh	102.9
Cobalt.....	Co	58.97	Rubidium.....	Rb	85.45
Columbium.....	Cb	93.1	Ruthenium.....	Ru	101.7
Copper.....	Cu	63.57	Samarium.....	Sa	150.4
Dysprosium.....	Dy	162.5	Scandium.....	Sc	44.1
Erbium.....	Er	167.7	Selenium.....	Se	79.2
Europium.....	Eu	152.0	Silicon.....	Si	28.3
Fluorine.....	F	19.0	Silver.....	Ag	107.88
Gadolinium.....	Gd	157.3	Sodium.....	Na	23.00
Gallium.....	Ga	69.9	Strontium.....	Sr	87.63
Germanium.....	Ge	72.5	Sulfur.....	S	32.06
Glucinum.....	Gl	9.1	Tantalum.....	Ta	181.5
Gold.....	Au	197.2	Tellurium.....	Te	127.5
Helium.....	He	4.00	Terbium.....	Tb	159.2
Hydrogen.....	H	1.008	Thallium.....	Tl	204.0
Indium.....	In	114.8	Thorium.....	Th	232.4
Iodine.....	I	126.92	Thulium.....	Tm	168.4
Iridium.....	Ir	193.1	Tin.....	Sn	118.7
Iron.....	Fe	55.84	Titanium.....	Ti	48.1
Krypton.....	Kr	82.92	W.....	W	184.0
Lanthanum.....	La	139.0	U.....	U	238.2
Lead.....	Pb	207.2	Vanadium.....	V	51.0
Lithium.....	Li	6.94	Xenon.....	Xe	130.2
Lutecium.....	Lu	175.0	Ytterbium.....	Yb	173.5
Magnesium.....	Mg	24.32	Yttrium.....	Yt	88.7
Manganese.....	Mn	54.93	Zinc.....	Zn	65.37
Mercury.....	Hg	200.6	Zirconium.....	Zr	90.6

